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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Application of Gelorme et Al : Art Unit Not Yet Assigned

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For: ELECTRICALLY CONDUCTING ADHESIVES  
FOR VIA FILL APPLICATIONS

TRANSMITTAL LETTER FOR  
PATENT APPLICATION

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

Please find enclosed the following Patent Application of  
Jeffrey D. Gelorme, Sung K. Kang, Kostas Papsthomas and Sampath Purushothaman

The application consists of :

Transmittal letter- 1 page  
Specification and claims -14 pages,  
Drawings 1 sheet- informal  
Filing Fee \$768 .00 - Check attached  
Information Disclosure Statement - 1 page + references

The filing fee is calculated as follows

Basic Fee	\$ 690.00
Total claims 13 - no extra	
Independent claims 4 - 3 = 1 extra	\$78.00
Total	\$768.00

Respectfully submitted,

*Alvin J. Riddles* 2/24/00  
Alvin J. Riddles  
Reg.No. 17862

## ELECTRICALLY CONDUCTING ADHESIVES FOR VIA FILL APPLICATIONS

### Field of the invention

The invention is in the field of electronic apparatus manufacturing of circuitry mounted on an insulating supporting backing, such as a printed circuit board, and in particular to the provision of a wider specification range conductive composition that can fill a hole through the insulating backing and can serve as an interconnection between circuitry on each side of the backing material.

### Background

Needs are developing in the control of cost and the downsizing of electronic packaging. The goals are to provide higher density, finer pitch and higher performance, all at lower cost. In the mounting of circuitry on an insulating backing, the standard in the art for interconnections or vias through the insulating backing has been the plated through hole. At this state of the art however, the plated through hole technology is encountering cost pressures and it has limits in how dense or tightly packed the circuitry can be.

The operations involved in manufacturing plated through holes or vias are expensive and are not readily adaptable to the future pad density requirements. The present plated through hole technology is approaching limits at about 20 pads or circuit node points per square centimeter. The needs of the technology indicate that a density of many times that will probably be required.

Efforts in the art to meet the density, pitch, performance and cost goals have been directed to a

technique called "built up multilayer" where the circuits involve a series of superimposed laminates of foil and insulator that are interconnected using fine pitch holes that are filled with conductive paste. The technique has been extensively discussed in the literature, an example being R. Lasky, *Electronic Packaging and Production*, April, 1998, pages 75 - 78. There are many variations. In general the technique can provide a density of greater than 100 pads per square centimeter.

The built up multilayer circuitry technique requires an electrically conducting paste that will be used to fill the many small holes or vias. The paste is also referred to in the art by the term adhesive. The electrically conductive paste must be thermally and reliably compatible with the fabrication and service specifications for the places where it is to be used. The paste, in general, has metal particles suspended in a vehicle, also known in the art by the terminology resin, that can be forced into a via hole through the insulator and when subjected to a curing type cycle, during which the vehicle solidifies with the metal particles in contact with each other forming an electrical path through the via between conductors on surfaces on each side of the insulator.

One such paste is described in U.S. Patent 5,652,042 where metal particles such as copper are suspended in an epoxy vehicle. The paste is squeegeed or doctor bladed into the via holes. There is a heat and pressure cycle that hardens the vehicle. The metal particles in contact with each other provide electrical interconnection.

Further work in paste technology involves introducing silver flakes into the vehicle, coating the metal particles with a low melting metal to produce metallurgical bonding of the metal particles,

and, the use of a screen printable paste of silver, copper and epoxy. Problems remain with such process properties as vehicle shrinkage in connection with change of state, and the corrosion and electromigration properties of the metals, especially pure silver and copper..

In Patent Applications, Ser. No. Filed (IBM Docket YO997-089)and Ser. No. Filed

( IBM Docket YO998-196) a technology is described of providing and using an alloy coated metal particle which broadens the metallurgical bond forming range thereby providing metallurgical bonds not only between the particles but also to the conducting pads.

As the art progresses, the specifications will become tighter and the process windows will become narrower, so that there will be a growing need for an ever broader range of properties and selection of metal particles and vehicle formulations.

#### Summary of the invention

Electrically conducting adhesives having a broader selectable range of properties are provided by having random sizes of micrometer diameter range particles of for example Cu, Ni, Co, Ag, Pd, Pt, polymer and ceramic each coated with a low melting temperature metal. The coated particles are suspended in a vehicle of a mixture of thermosetting resins together with a flux resin, selected for viscosity and low shrinkage, for screen printability, for electrical and for mechanical properties over a broad range of specification conditions. The vehicle or resin system includes thermosetting cyclo-aliphatic epoxy, thermosetting phenoxy polymer, thermosetting mono-functional limonene

oxide and flux. The low temperature melting coating system for the particles includes In, Sn, and alloys such as In-Sn, Sn-Pb, Bi-Sn, Bi-Sn-In and InAg.

#### Brief description of the drawings

Figure 1 is a cross sectional depiction of a single random size micrometer diameter range coated particle.

Figure 2 is a cross sectional depiction of the metallurgical bonds at the tangential contacting area between coated particle intersections and particle and conductor intersections.

Figure 3 is a compilation of the properties and performance of example formulations of the invention in comparison with a commercially available prior art type of formulation.

#### Description of the invention

An improved electrically conducting adhesive is provided that can be pressed into a via hole in an insulating layer of a to be circuit member and upon curing will have a metallurgical conductive path between surfaces of the insulating layer and a metallurgical bond to conductive members on those surfaces. The adhesive is in paste form as pressed into the hole into the insulating layer. It is solidified in a curing cycle involving heat and pressure.

The electrically conducting adhesive of the invention uses random sizes of micrometer diameter range particles of for example Cu, Ni, Co, Ag, Pd, Pt, polymer and ceramic each coated with a low melting temperature metal. The heat in the curing cycle is of the order of the melting

temperature of the coating metal. In the heat and pressure curing cycle the particles join, where there is tangential surface touching, to form fused or diffused metallurgical bonds. The coated particles are suspended in a physical binder or vehicle that is a mixture of thermosetting resins together with a flux resin, selected so that the binder or vehicle and particle combination will have low and selectable viscosity before curing and low shrinkage through the curing cycle and in service. The binder or vehicle is a resin system that includes thermosetting cyclo-aliphatic epoxy, flux, thermosetting phenoxy polymer and may include thermosetting mono-functional limonene oxide. The low temperature melting coating system for the particles includes In, Sn, In-Sn, Sn-Pb, Bi-Sn, Bi-Sn-In and InAg. The electrically conducting adhesive of the invention has improved electrical and mechanical properties over a broad range of specifications and improved viscosity in the pre cured state for such operations as screen printing.

The invention is illustrated by using BiSn as an example for the low melting temperature coating and Cu as the random micrometer range particles. The BiSn alloy is plated on the Cu particles which are in the 5 -7 micrometer diameter range. The plating can be accomplished in a plating bath associated with a ball milling type operation as described in Patent Applications, Ser. No. Filed (IBM Docket YO997-089) and Ser. No. Filed (IBM Docket YO998-196). The

resulting particles are depicted in Fig. 1. Referring to Fig. 1 there is shown a 5 - 7 micrometer range Cu particle 1 having a surface coating 2 of the BiSn alloy low melting temperature coating.

In accordance with the invention the low temperature melting alloy coating 2 imparts a number of specification accommodating advantages. Considering that a regular solder coating would melt at about 215 degrees C, the BiSn eutectic alloy would provide a lower melting temperature of 140

degrees C. with selectable melting temperature values above by alteration of the two alloy ingredient proportions thus providing ability to meet new process window specifications. The BiSn alloy coating 2 also provides corrosion resistance for the Cu particles.

A quantity of powder of the BiSn coated Cu particles is placed in a vehicle or resin system forming a paste that is pressed into via holes through the insulating circuit backing as depicted in Fig.2., Referring to Figure 2 a cross sectional depiction is provided of the hole 3 at the surface 4 of the insulator 5 illustrating that the coating 2 on each particle forms a fused metallurgical bond 6 at each tangential contact with adjacent particles and with the conductor 7 on the surface 4. The metallurgical bond can be by solid state bonding or by liquid - solid bonding under the heat and pressure curing cycle. A satisfactory heat cycle would be 150 degrees C. for 30 minutes. A satisfactory pressure cycle would be to apply 500 pounds per square inch for the duration of the heat cycle.

The vehicle or resin system is solvent free and is formulated by mixing thermosetting resins such as cyclo-aliphatic type epoxy, phenoxy polymer, and mono-functional limonene oxide together with a flux resin. The limonene oxide ingredient permits variation of the viscosity of the paste. Viscosity selectability is highly useful in conditions where the aspect ratio of a hole into which the paste must be pressed is high and where screen printing is involved in the manufacturing process. The flux ingredient improves the metallurgical bond between the particles and with the conductors on the surface of the insulator.

The specification variation and processing variation flexibility of the invention are illustrated in



Fig 3 which is a compilation of properties and performance of four example formulations of the invention identified as BiSn48, BiSn49, BiSn53 and BiSn 54; in comparison with a standard commercially available prior art type formulation identified as AgCu01.

The electrical and mechanical properties of all the invention examples and the prior art example are established using a standard in the art joint testing technique as described in the technical article "Development of High Conductivity Lead (Pb)-Free Conducting Adhesives" by Kang et al, in IEEE Transactions on Components, Packaging and Manufacturing Technology, Part A, Volume 21, No.1 pages 18 - 22 at page 20 thereof.

Referring to Figure 3 the following observations are advanced.

The electrical and mechanical properties values of the BiSn49, BiSn53 and BiSn54 examples are superior to the commercially available example AgCu01.

Where the insulator is relatively thick, for example about 0.105 inch thick having a hole diameter of 0.010 inch so that the aspect ratio would be 10 or higher; for the hole to be completely conductively filled, the formulations of examples BiSn49 and BiSn54 would be required. A carrier film with a 0.004 inch thick coating of paste may be used in laminating under heat and pressure.

Where the insulator is relatively thin, for example about 0.024 inch thick having a hole diameter of 0.008 inch so that the aspect ratio would be 3, a formulation of paste with medium flow characteristics as provided by the example BiSn48 would be best.

Satisfactory materials as listed in the resin % column of Fig. 3 may be acquired from the following:



YO999-510

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Cyclo-Aliphatic Epoxy Resin is supplied by Union Carbide Inc.

under the designation (ERL-4221E).

(+) Limonene Oxide ( a mixture of cis and trans)is supplied by Aldrich Chemical Co.

under the designation of (21,832 - 4)

The phenoxy resin is Paphen(TM) phenoxy resin is supplied by Phenoxy Specialties Co.,

under the designation PKHC(TM)(CAS)25068-38-6

The No Clean Flux is supplied by Qualitek International Inc.,

under the designation Qualitek #305 flux.

What has been described is a conductive adhesive technology involving combined particle coating and vehicle formulation that imparts flexibility in meeting manufacturing specifications.

What is claimed is:

- 1        1. In electronic apparatus manufacturing wherein conductive paths through an insulating  
2        layer is used to contact at least one circuitry node pad on at least one surface of the insulating  
3        layer, and the conductive paths are formed by placing an adhesive paste of coated particles  
4        suspended in a vehicle in at least one via hole in at least one insulating layer,  
5        the improvement method comprising the serial combination of the steps of:  
6        providing of an adhesive paste,  
7        said adhesive paste having random sizes of micrometer diameter range particles each coated  
8        with a low melting temperature metal suspended in a vehicle of a mixture of  
9        thermosetting resins together with a flux resin selected for viscosity and low shrinkage,  
10       introducing said adhesive paste into said at least one via hole in said at least one insulating  
11       layer, and,  
12       subjecting the combination of said adhesive paste in said at least one via hole in said at least  
13       one insulating layer to a vehicle curing cycle including heat of the order of said low  
14       melting temperature of said metal and pressure.
- 1       2. The improvement method of claim 1 wherein said random sizes of micrometer diameter  
2       range particles are in the range of 5 -7 micrometers of a material selected from the  
3       group of Cu, Ni, Co, Ag, Pd, Pt, polymer and ceramic.
- 1       3. The improvement method of claim 1 wherein said low melting temperature metal is a  
2       material taken from the group of In, Sn, In-Sn, Sn-Pb, Bi-Sn, Bi-Sn-In and InAg.

1        4. The improvement method of claim 1 wherein said thermosetting resins in said vehicle  
2            are taken from the group of cyclo-aliphatic epoxy, phenoxy polymer, and,  
3            mono-functional limonene oxide.

1        5. The improvement method of claim 3 wherein said thermosetting resins in said vehicle  
2            are taken from the group of cyclo-aliphatic epoxy, phenoxy polymer, and,  
3            mono-functional limonene oxide and a flux.

1        6. The improvement method of claim 1 wherein said particles are of Cu, said low melting  
2            temperature metal is Bi-Sn and said thermosetting resins in said vehicle  
3            are taken from the group of cyclo-aliphatic epoxy, phenoxy polymer,  
4            monofunctional limonene oxide and a flux.

1        7. The improvement method of claim 1 wherein said particles are of Cu, said low melting  
2            temperature metal is Bi-Sn and said thermosetting resins in said vehicle  
3            are taken from the group of cyclo-aliphatic epoxy, phenoxy polymer,  
4            and a flux.

1        8. In electronic apparatus manufacturing wherein conductive paths through an insulating  
2        layer is used to contact at least one circuitry node pad on at least one surface of the insulating  
3        layer, and the conductive paths are formed by placing an adhesive paste of coated particles  
4        suspended in a vehicle in at least one via hole in at least one insulating layer,  
5        the improvement method comprising the serial combination of the steps of:  
6        providing of an adhesive paste,

7 said adhesive paste having random sizes of 5 -7 micrometer diameter range Cu particles  
8 each coated BiSn suspended in a vehicle of a mixture of cyclo-aliphatic epoxy, phenoxy  
9 polymer, mono-functional limonene oxide and a flux,  
10 introducing said adhesive paste into said at least one via hole in said at least one insulating  
11 layer, and,  
12 subjecting the combination of said adhesive paste in said at least one via hole in said at least  
13 one insulating layer to a vehicle curing cycle including heat of the order of said low  
14 melting temperature of said metal and pressure.

1 9. In electronic apparatus manufacturing wherein conductive paths through an insulating  
2 layer is used to contact at least one circuitry node pad on at least one surface of the insulating  
3 layer, and the conductive paths are formed by placing an adhesive paste of coated particles  
4 suspended in a vehicle in at least one via hole in at least one insulating layer,  
5 the improvement method comprising the serial combination of the steps of:  
6 providing of an adhesive paste,  
7 said adhesive paste having random sizes of 5 -7 micrometer diameter range Cu particles  
8 each coated BiSn suspended in a vehicle of a mixture of cyclo-aliphatic epoxy, phenoxy  
9 polymer, and a flux,  
10 introducing said adhesive paste into said at least one via hole in said at least one insulating  
11 layer, and,  
12 subjecting the combination of said adhesive paste in said at least one via hole in said at least  
13 one insulating layer to a vehicle curing cycle including heat of the order of said low

14 melting temperature of said metal and pressure.

1 10. In electronic apparatus manufacturing wherein conductive paths through an insulating  
2 layer is used to contact at least one circuitry node pad on at least one surface of the insulating  
3 layer, and the conductive paths are formed by placing an adhesive paste of coated particles  
4 suspended in a vehicle in at least one via hole in at least one insulating layer,  
5 the improvement method comprising the serial combination of the steps of:  
6 providing of an adhesive paste,  
7 said adhesive paste having random sizes of 5 -7 micrometer diameter range Cu particles  
8 each coated BiSn suspended in a vehicle of a mixture of cyclo-aliphatic epoxy, phenoxy  
9 polymer, mono-functional limonene oxide and a flux,  
10 introducing said adhesive paste into said at least one via hole in said at least one insulating  
11 layer, and,  
12 subjecting the combination of said adhesive paste in said at least one via hole in said at least  
13 one insulating layer to a vehicle curing cycle including heat of the order of said low  
14 melting temperature of said metal and pressure.

1 11. The improvement method of claim 9 wherein said mixture of cyclo-aliphatic epoxy,  
2 phenoxy polymer, and a flux is in a proportion of epoxy 86%, phenoxy polymer 10%  
3 and flux 4 %.

1 12. The improvement method of claim 10 wherein said mixture of cyclo-aliphatic epoxy,

1        13. The improvement method of claim 10 wherein said mixture of cyclo-aliphatic epoxy,  
2        phenoxy polymer, mono-functional limonene oxide and a flux is in a proportion of  
3        epoxy 4%, phenoxy polymer 4%, mono-functional limonene oxide 88%, and flux 4%.

## ELECTRICALLY CONDUCTING ADHESIVES FOR VIA FILL APPLICATIONS

## ABSTRACT

Electrically conducting adhesives having a broader selectable range of properties are provided by having random sizes of micrometer diameter range particles coated with a low melting temperature metal. The coated particles are suspended in a vehicle of a mixture of thermosetting resins together with a flux resin selected for viscosity and low shrinkage, for screen printability, for electrical and for mechanical properties over a broad range of specification conditions. The vehicle or resin system includes thermosetting cyclo-aliphatic epoxy, thermosetting phenoxy polymer and thermosetting mono-functional limonene oxide. The low temperature melting coating system for the particles includes In, Sn, and alloys such as In-Sn, Sn-Pb, Bi-Sn-In and InAg. The micrometer diameter range particles includes Cu, Ni, Co, Ag, Pd, Pt, polymer and ceramic.



**An Apparatus and Method for Plating Coatings on to Fine Powder****Materials and Use of the Powder Therefrom**

S. K. Kang, and S. Purushothaman

**FIELD OF THE INVENTION**

The present invention is directed to a method of producing metal powders useful in pastes for forming electroconductive connections between electroconductive members, and methods of use of the same in electronic applications.

**BACKGROUND**

Most electrical conductors used in electronic devices are made of metals, such as copper, aluminum, gold, silver, lead/tin (solder), molybdenum and others. Solder connection technology using lead/tin alloys plays a key role in various levels of electronic packaging, such as flip-chip connection (or C4), solder-ball connection in ball-grid-arrays (BGA), and IC package assembly to a printed circuit board (PCB). Solder joints produced in the electronic packages serve critically as electrical interconnections as well as mechanical/physical connections. When either of the functions is not achieved, the solder joint is considered to have failed, which can often threaten a shut-down of the whole electronic system.

When microelectronic packages are assembled to a printed circuit board, the lead-tin eutectic solder, 63%Sn-37%Pb, having the lowest melting point (183 °C) among Pb-Sn

alloys, is most widely used. In these applications, there are two solder connection technologies employed for mass production: plated-through-hole (PTH) and surface mount technology (SMT) soldering. The basic difference between the two technologies originates from the difference in the PCB design and its interconnection scheme.

In SMT soldering, microelectronic packages are directly attached to the surface of a PCB. A major advantage of SMT is high packaging density, which is realized by eliminating most PTH's in the PCB as well as by utilizing both surfaces of the PCB to accommodate components. In addition, SMT packages have a finer lead pitch and a smaller package size compared to traditional PTH packages. Hence, SMT has contributed significantly in reducing the size of electronic packages and thereby the volume of the overall system.

In SMT soldering, solder paste is applied to a PCB by screen printing. Solder paste consists of fine solder powder, flux, and organic vehicles. During the reflow process, solder particles are melted, flux is activated, solvent materials are evaporated, and simultaneously molten solder coalesces and is eventually solidified. In contrast, in the wave soldering process, a PCB is first fluxed and components are mounted on it. Then it is moved over a wave of molten solder.

The soldering process is usually completed by subjecting the solder joints to a cleaning step to remove residual flux materials. Due to environmental concerns, CFCs (chlorofluoro carbons) and other harmful cleaning agents used for this purpose are being eliminated and water-soluble or no-clean flux materials are being used to minimize or eliminate the cleaning steps.

Recent advances in microelectronic devices demand a very fine pitch connection between electronic packages and a printed circuit board (in an order of a few hundred micrometer pitch). The current solder paste technology used in SMT can not handle this very fine pitch interconnection due to the soldering defects such as bridging or solder balling. Another technical limitation of using the Pb-Sn eutectic solder is its high reflow temperature, approximately 215 °C. This temperature is already higher than the glass transition temperature of the epoxy resin used in most polymeric printed circuit board materials. Thermal exposure at this reflow temperature produces significant thermal strains in a printed circuit board after soldering, especially in the direction perpendicular to the surface of a PCB, because no structural reinforcement is made in that direction. Thereby, the residual thermal strains in an assembled PCB could significantly degrade the reliability of an electronic system.

A more serious concern regarding the usage of lead (Pb)-containing solders is an environmental issue, a trend already experienced in other industries and has led to the elimination of lead from gasoline and paints.

In the electronic industry, two different groups of materials are investigated currently for the possibility of substituting the Pb-containing solder materials; Pb-free solder alloys, and electrically conductive pastes (ECP). The present invention discusses the development and applications of the electrically conductive paste materials. An electrically conductive paste (or adhesive) is made of metallic filler particles loaded in the matrix of a polymer material. The polymer matrix can be any polymer suitable for use in a paste, for example, a thermoplastic or thermoset. The polymer is selected preferably from the group comprising epoxy, polyester and polyimide. The soluble epoxy, in particular, soluble ketal and acetal diepoxides, as described in U.S. application serial

no. 08/210,879, the teaching of which is incorporated herein by reference can also be used as the polymer matrix. Referring to Fig. 1, silver-particle 2 filled epoxy 4 is the most common example of the electrically conductive pastes 6, schematically shown therein as disposed between surface 8 and surface 10. The silver particles usually in the shape of flakes provide electrical conduction by percolation mechanism, while the epoxy matrix provides adhesive bond between the components and a substrate. This silver-filled epoxy material has been long used in the electronic applications as a die-bonding material, where its good thermal conduction rather than electrical conduction property is utilized. However, this material has not been accepted for the applications requiring high electroconduction and fine pitch connection. The silver-filled epoxy material has several limitations, such as low electrical conductivity, increase in contact resistance during thermal exposure, low joint strength, silver migration, difficulty in rework, and others. Since this silver-filled epoxy material is electrically conductive in all the directions, it is classified as "isotropic" in electro- conduction. There is another class of electrically conductive adhesive (or film), which provides electroconduction only in one direction. This class of the materials is known as "anisotropic" conductive adhesive film 12, shown schematically in FIG. 2A, which contains electrically conductive particles 14 in a binder or adhesive material 16. The anisotropic conductive adhesive or film 12 becomes conductive only when it is compressed between two conducting surfaces 18 and 20 as shown in FIG. 2B. This process normally requires heat and pressure. The major application of the anisotropic conductive film is for joining of a liquid crystal display panel to its electronic printed circuit board. The conducting particles 14 are usually deformable, such as solder balls, or plastic balls coated with nickel and gold. The binder or adhesive material 16 is mostly a thermosetting resin.

The ECP made of Sn-plated Cu powder and polyimide-siloxane resin disclosed in our earlier patent application, YO994-097, is a good candidate for the high temperature solder joints such as controlled collapse chip connections (C4) and solder ball connection (SBC) to a ceramic substrate. However, for the polymeric printed circuit board applications, this ECP is not adequate, because the reflow temperature such as 250 °C is much higher than the glass transition temperature of the polymeric resin, for example, FR-4. Candidates for this purpose are ECP's made of Cu powder plated with Indium, tin-bismuth alloys or Indium-tin alloys, formulated with polyimide-siloxane resin. The reflow temperature of these powder pastes is expected to be between 120 and 180 °C, which is even lower than the reflow temperature of the Pb/Sn eutectic solder, 215 °C.

In an earlier patent application YO994281 dated March 31, 1995, we have disclosed a process to produce dendritic copper powder overcoated with Sn or Sn and BiSn coatings by electrolytic plating on a rigid inert cathode. The morphology of the powder that can be made by this technique is restricted to the dendritic shape which is not always the preferred one for all ECP applications.

A solder/polymer composite paste material is disclosed in U. S. Pat. No.5,062,896 (Huang et. al.), comprising a major proportion of a meltable solder powder filler, such as Bi-Sn, Pb-Sn, Bi-Sn-Pb alloys, a minor proportion of a thermoplastic polymer such as a polyimide siloxane, and a minor proportion of a fluxing agent. An oxide-free, partially coalesced solder alloy connection is obtained, which is polymer strengthened and reworkable at a low reflow temperature, per se, or in the presence of polymer solvent.

In U. S. Pat. No.5,286,417 (Mahmoud et. al.), a fusible conductive adhesive is disclosed, which comprises metal alloy fillers such as Sn-Au and Bi-Au, and a thermoplastic polymer having a glass transition temperature overlapping the melting temperature of the metal filler alloys. The loading of the conductive material in the polymer is in the range of about 15% to about 20% by weight.

In U. S. Pat. No.5,136,365 (Pennisi et. al.), an adhesive material is disclosed, which contains a fluxing agent and metal particles for use in reflow soldering such as Sn, Pb, In, Bi, Sb, Ag and others, in the matrix of an epoxy resin. Upon reflow soldering, the said adhesive forms anisotropic electroconduction between an electrical component and a substrate.

In U. S. Pat. No.5,213,715 (Patterson et. al.), a directionally conductive polymer is disclosed, which contains a metallic filler powder of Ni or Cu. The metallic powder is treated by a different polymer than the polymer used as a matrix resin. Upon compression, the coated polymer dissolves to make an electrical conduction among the filler particles.

In a previous patent application Docket YO997-089, we have disclosed a method to plate fine powder materials using a shaker plating method wherein the powder is placed in contact with a cathode surface and moved over it by a shaking action during the plating process.

#### OBJECTS

It is an object of the present invention to coat free standing metallic powder of any desired shape, morphology and size with a surface coating of a metal or an alloy by electroplating.

It is another object of this invention to provide a plating apparatus and method that can be scaled up to produce large batches of coated powder.

It is yet another object of the present invention to provide a method of fabricating an electrically conductive paste material which is environmentally safe and low cost.

It is another object of the present invention to provide a method of fabricating an electrically conductive paste material which produces a higher electrical conductivity than the conventional silver-filled epoxy does.

It is another object of the present invention to provide a method of fabricating an electrically conductive paste material which can be processed at a lower temperature than the reflow temperature of Pb-Sn eutectic solder paste.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Further objects, features, and advantages of the present invention will become apparent from a consideration of the following detailed description of the invention when read in conjunction with the drawing FIGs., in which:



FIG. 1 is a schematic illustration of an electrically conductive paste comprising silver flake particles as a filler in the matrix of epoxy resin. The conductive paste is classified as isotropic in electroconduction.

FIG. 2 is a schematic illustration of an electrically conductive adhesive which becomes electrically conductive only in the one direction when the adhesive film is compressed between two contact or bond pads. The conductive adhesive (or film) is classified as anisotropic.

FIG. 3 is a schematic illustration of an electrically conductive paste material, comprising spherical copper powder filled in the matrix of thermoplastic polymer resin. The copper particles are coated with a low melting point, non-toxic metal such as tin, indium, bismuth, antimony or combinations thereof.

FIG. 4 is a schematic illustration of the apparatus used to electrolytically deposit thin metal or alloy coatings on fine copper powder.

FIG. 5 is a differential scanning calorimeter (DSC) scan of the SnBi plated copper powder showing the three distinct melting processes that occur in the coating layer.

FIG. 6 is an x-ray diffractogram of the SnBi plated copper powder showing the presence of peaks characteristic of crystalline copper, tin and bismuth.

## SUMMARY OF THE INVENTION

A broad aspect of the present invention is a method including the steps of disposing a powder with a conducting surface in a plating solution contained in a barrel cell which is impermeable to the powder and selectively permeable to the plating solution and the ions contained therein; providing a cathode contact ball; further providing a multiplicity of conducting spheres in the same cell to facilitate extended electrical contact between the cathode ball and the powder; disposing the said barrel in a bigger anode container filled with a second electrolyte; disposing an anode in the said anode chamber; providing a means to turn the barrel on its axis so as to produce a tumbling action to ensure mixing and contact of the powder particles with the conducting spheres and the cathode ball; applying an electrical potential such that the anode is positive with respect to the cathode to set up current flow through the electrolyte and the permeable cell wall to facilitate electrolytic plating of the desired coating from the solution on to the powder particles.

A second aspect of the present invention is to produce a powder with two or more layers applied by successive combinations of electroless plating and electroplating as described in the preceding paragraph to achieve a more versatile combination of coating properties.

In a more particular aspect of this invention, the coated powder and the conducting spheres are separated from the solution, rinsed, subjected to tumbling in a ball mill to recover the coated powder from the said spheres and dried and used to formulate electrically conducting adhesives by mixing with a polymer resin dissolved in a suitable solvent.

#### DETAILED DESCRIPTION

According to an embodiment of the present invention, an electrically conductive paste (ECP) material is disclosed, which consists of copper powder coated with a thin layer of low melting point, Pb-free metals selected from Sn, In, Bi, Sb and their alloys, mixed with an environmentally-safe fluxing agent, and dispersed in the matrix of thermoplastic or thermosetting polymers. The microstructure of the ECP containing SnBi coated Cu powder is shown schematically in a cross-section view in FIG. 3.

In one particular embodiment, we disclose a new electrically conductive paste material consisting of copper powder coated with a tin bismuth alloy, polyimide-siloxane, solvent (acetophenone or n-methyl pyrrolidone) and a carboxylic acid/surfactant. The tin/bismuth coated copper powder is produced by simultaneous electrodeposition of tin and bismuth atoms as an alloy from a commercial electroplating solution produced by Lea Ronal Corporation using the special apparatus illustrated in Fig. 4.

The apparatus comprises a cathode container 40 predominantly made of a nonconductive material such as polypropylene, high density polyethylene or the like, provided on at least part of the wall surface 45 with a separate membrane or a chemical modification of the container wall such that electrolytic solutions can permeate through that area while powder particles bigger than about 2 micrometers diameter cannot. A polymer filter membrane with pore diameters less than 2 micrometers could be used for this purpose as item 45. A preweighed amount of conductive powder 49 to be coated is placed in the cathode chamber and the container is filled with a suitable electroplating solution 44 (in this case a SnBi plating solution) so as to partially fill the cathode chamber. Additionally, a quantity of conducting spherical balls 48 are added to the solution 44. The spheres 48 are required to be resistant to attack by the plating solution

and are typically made of stainless steel alloy 304, 410 or the like and are about 3 mm in diameter. The quantity of these spheres is determined experimentally to optimize the process as described later. The cathode barrel so filled is mounted on a rotary assembly 53 by means of a cap 43. The rotary assembly 53 is provided with a motor 50 that drives the gear assembly 54 that can turn the cathode container about its axis at a desired rate. The cap 43 is provided with an axial feedthrough 55 that acts as a conduit for connecting in the negative electrical terminal 51 to the cathode ball 47 through the insulating connecting wire 56. The cathode ball can be made of the same material as the spheres 48. The axial feed allows the cathode chamber to turn without twisting the cathode connection wire 56. The whole cathode assembly can be mounted at any desired angle with respect to the horizontal in order to facilitate powder flow within the cell during the rotation of the cathode chamber. The cathode assembly is placed at a slight angle (from 1 to 10 degrees) to the horizontal and immersed into a bath of electroplating solution in a second chamber 41 designated the anode chamber. An anode 46 is placed in the anode chamber 41. In the present application anode 36 is made of pure tin sheet. Anode 46 connected by a suitable wire to the positive terminal 52.

The anode and cathode leads 52 and 51 are connected to the positive and the negative legs, respectively, of a dc power supply (for example Kepco Model JQE 0 to 6V/ 0 to 20 Amps). The cathode chamber is rotated about its axis using the motor and gear assembly and a dc voltage is applied across the positive 52 and negative 51 terminals causing a current to flow through the cell and plating to occur in the conducting surfaces in the cathode chamber. By ensuring that the quantity of spheres 48 is sufficient to ensure dispersion of the powder 49 and to allow continued contact between the cathode ball 47 and the powder 49, a steady plate up of a coating on the powder surface is achieved.

After the plating is performed for the requisite period of time, the dc power is switched off, the cathode chamber is removed from the cap and the solution decanted from the chamber. The coated powder and the spheres are then rinsed in deionized water and a suitable solvent such as isopropanol. The sphere/powder mixture is then transferred to a small ball mill, Spex mixer/mill 8000 (Spex Industries, Inc., Edison, NJ), along with a small volume of the solvent and subjected to ball milling for a period of few minutes. This enables the separation of any powder attached to the spheres and causes separation of any agglomerated powder mass. Powder and the spheres are dried and separated readily by sieving.

The copper powder may be substituted with others such as nickel, cobalt, silver, palladium, platinum depending on the specific application. Alternatively, one can also use powder that is nonconducting in the bulk but provided with an electrically conductive surface layer. Metallized ceramic or polymer powder is a typical example of this class of materials. The tin/bismuth alloy coating can be replaced by other metals such as Sn, In, Zn, Pb, Bi and Sb or their alloys. Because the process can start with any powder size or aspect ratio, a wide variety of coated filler powders can be prepared.

When such a powder is formulated into an ECP, a joining operation can be performed near the melting point of Sn/Bi alloy which is about 140°C resulting in sound metallurgical bonding between the particles themselves and between the particles and substrate contact pad surfaces on electronic devices and cards which are typically made of copper, copper/gold, nickel, nickel/gold, nickel/palladium, palladium, or palladium/gold.

Alternately, a coating of indium (melting point 159°C) or an alloy of indium and tin (melting point 120 °C) can be used as coatings on the copper particles to obtain bonding

as described above. Since indium alloys have acceptable wettability on even hard to solder metals such as aluminum, titanium, molybdenum, or tungsten, the present invention material can be used as fillers in ECP's for joining of liquid crystal display devices. The joining process can be either solid-state or liquid-solid reaction. The polymer curing process can be combined with the joining process depending on the paste formulation so that both these can be achieved in a single bonding cycle. Because of the metallurgical bonding and the high conductivity copper core, a higher electrical conductivity is expected with the joints made of the new paste material than with those of the silver-epoxy material. The metallurgical bonds also provide stable electrical conductivity of the new joints upon thermal exposure and cycling. It is also expected to have a higher joint strength from the combined effect of the metallurgical and adhesive bonds. It should be noted that such bonding is achieved at significantly lower temperatures than what is currently practiced for PbSn eutectic solder assemblies (215°C) thereby reducing the thermal stresses and the associated warpage that may occur in card substrates.

In another variant of the coating composition a low melting temperature and uniform coverage can be achieved in the following manner. A coating of a thin layer of Sn can be applied by electroless plating first on the copper powder as described in our earlier application, YO994-097. This is followed by electroplating the SnBi alloy as described in the present invention. The combination would ensure complete coverage of all copper surfaces and provide a low melting coating alloy. In a more general variant, the coating can be any metal or alloy that can be coated on the powder by an electroless or electrolytic plating, with additional coating of metal or alloy that can be applied by electrolytic or electroless plating with the combination providing the desired lower melting point alloy.



The polymer component of the paste can be polymer resins prepared from renewable resources or bio-based materials after appropriate functionalization to achieve the desirable thermal and rheological properties. Lignin (by product from paper manufacture), cellulose, wood or crop oils are potential candidates for this purpose. Use of these materials is environmentally preferable because they are derived from natural and renewable resources and can be disposed of more readily at the end of the useful life of the electronic assembly. This is particularly attractive because the use of the coated copper powder as filler eliminates the use of lead (Pb) containing solders and the resulting paste formulation is non-toxic and easy to dispose.

Our previous application, Serial #326,626 filed on October 24, 1994, the teaching of which is incorporated herein by reference teaches using tin-coated copper powder as a filler material in formulating an electrically conductive paste. The copper powder has a spherical morphology, which can be produced by either powder atomization or electrodeposition process. Tin coating is performed on copper powder by using an electroless immersion Sn plating solution.

Since there is no commercial immersion plating process available for many of the coating metals of interest, specifically indium, bismuth and antimony, coating of copper powder by a process similar to tin-coating on copper powder described above is not possible.

The process and structure of the present invention provides the solution to the above problems through an electroplating method to coat In, Bi, Sb, Sn and Pb or alloys



thereof on free standing powder particles. The method is also applicable to other metal coatings that cannot be obtained easily by electroless plating.

### **Example 1**

About 5 gms of copper powder nominally 5 to 10 micron diameter supplied by SCM Metals Corporation, Research Triangle Park, NC, was presoaked in about 30 ml of SnBi alloy plating solution purchased from LeaRonan Corporation to remove the native surface oxide, as well as to prewet the surface. The mixture was transferred to the cathode chamber of our apparatus along with 20 gms of stainless steel spheres 0.125" diameter were added. An additional 400 ml of the plating solution was added to the cathode chamber and the contents were stirred together. The cathode chamber was then attached to the rotary assembly ensuring that the cathode ball was in place within the cathode chamber and in contact with the bed of stainless steel spheres. This cathode assembly was then placed within an outer plexiglass tank containing about 3 liters of the Sn Bi plating solution and a 0.125" thick tin (99.99% pure) sheet anode. The cathode chamber was set up so that it was at a tilt of about 5 to 10 degrees from the horizontal. It was ensured that the liquid level within the cathode chamber was below that in the outer tank in order that influx of solution from the outer tank can be facilitated. The gap between the anode sheet at the bottom of this anode tank and the cathode chamber was about 10 to 15 mm. The motor of the rotary assembly was set to turn the cathode assembly at about 20 rpm. Connections were made from the cathode lead to the negative terminal and the anode lead to the positive terminal of a dc power supply (Kepco JQE 0 to 6V, 0 to 20A) and plating was started. A nominal current of 5A was achieved while the cell voltage varied from 2 to 5 V as the cathode chamber turned. Plating was carried out for 30 minutes. The power supply was turned off, the leads disconnected, and the plating cell disassembled. The used plating solution was pipetted out, the powder and

the spheres rinsed thoroughly in deionized water and isopropanol to eliminate any residual plating chemicals. The mixture was then scooped out of the cathode chamber and subjected to ball milling in isopropanol medium. The spheres and plated powder were then dried and separated by sieving. Particles of plated powder in the 5 to 30 micrometer range were then collected for further analysis.

A small sample of the powder (usually 10 mg) was loaded into a Model SSC/5200 differential scanning calorimeter (DSC) made by Seiko Inc.. The sample was heated at a rate of 10 degrees C per minute from room temperature to 350C to monitor the melting processes that occur in the material. Fig. 5 shows a typical DSC scan indicating a major endothermic peak around around 140°C, which corresponds to the BiSn eutectic composition. In addition, there are two minor endothermic peaks corresponding to a off-eutectic bismuth rich SnBi alloy that melts at 200°C and the pure bismuth phase at 270°C. It is important to note that the surface coating has an incipient melting point of 140 C.

A small amount of the plated powder was sprinkled on a glass slide with a double stick adhesive tape on it, to make a thin bed of powder. The sample was then loaded in to a Philips X-ray diffractometer and a  $2\theta$  x-ray diffraction scan was performed to identify characteristic peaks of the crystalline phases in the powder. A typical scan shown in Figure 6, indicates that diffraction peaks corresponding to Cu, Sn and Bi are present and the copper coverage by the SnBi coating is good. Thus it was concluded that the above described procedure produces fine copper powder overcoated with a SnBi alloy layer with a lowest melting point of 140 C.

### Example 2

The BiSn-plated copper powder was used to formulate a conducting paste by mixing with polyimide siloxane resin dissolved in a solvent of NMP, acetophenone, or ethyl benzoate, and a no-clean flux, FLUX305, from Qualitek International, Inc., Addison, IL. The relative amount of the filler powder over the polymer resin varied from 30 to 90% in weight, depending on a specific application. To insure uniform dispersion of the ingredients, the mixture was processed in a three-roll shear mill. When the filler weight percent is low, a solvent drying process, for example, 100 °C, 1 h, is required to adjust the viscosity of the paste before dispensing the paste on to a desired foot print.

In order to characterize the electrical and mechanical properties, model joint samples made of the BiSn-plated filler conductive paste were manufactured by laminating two "L-shaped" copper coupons. The lamination was performed at a temperature slightly above the melting point of BiSn coating, for example, 180 °C, at a pressure of 25 psi. Contact resistance of the model joints were measured by four point probe method. The contact resistance values from a nominal joint area of 1.25 mm in diameter ranged from 1.4 to  $4.0 \times 10^{-4} \Omega$ . These values were equivalent to those of the model joints made with a commercial Ag-filled conductive paste.

The shear strength of the model joints made of the BiSn-plated powder was in the range of 5.7 to 8.2 lb, which was comparable to or better than those of the commercial paste.

### **Example 3**

The BiSn-plated copper powder was used to formulate a conducting paste by mixing with phenoxy polymer or styrene allyl alcohol dissolved in a solvent of NMP, acetophenone, ethyl benzoate, or propylene glycol methyl ether acetate (PGMEA), and

a no-clean flux. The relative amount of the filler powder over the polymer resin varied from 30 to 90% in weight, depending on a specific application. To insure uniform dispersion of the ingredients, the mixture was processed in a three-roll shear mill. When the filler weight percent is low, a solvent drying process, for example, 100 °C, 1 h, is required to adjust the viscosity of the paste before dispensing the paste on to a desired foot print.

In order to characterize the electrical and mechanical properties, model joint samples made of the BiSn-plated filler conductive paste were manufactured by laminating two "L-shaped" copper coupons. The lamination was performed at a temperature slightly above the melting point of BiSn coating, for example, 180 °C, at a pressure of 25 psi. Contact resistance of the model joints were measured by four point probe method. The contact resistance values from a nominal joint area of 1.25 mm in diameter ranged from 0.8 to  $2.4 \times 10^{-4} \Omega$ . These values were better than those of the model joints made with a commercial Ag-filled conductive paste.

The shear strength of the model joints made of the BiSn-plated powder was in the range of 8.3 to 10.5 lb, which was much better than those made of the commercial paste.

While the present invention has been described with respect to preferred embodiments, numerous modifications, changes, and improvements will occur to those skilled in the art without departing from the spirit and scope of the invention.

## CLAIMS

What is claimed is:

1. A method comprising the steps of:

providing an electrically nonconductive cathode chamber with at least part of its wall area rendered permeable to ions and electrolytic solutions;

premixing a predetermined quantity of a fine electroconductive powder and a first electroplating solution;

filling said cathode chamber with the said powder mixture and a plurality of electroconductive spheres;

disposing an electroconductive cathode ball in contact with said spheres and powder particles;

securing the said cathode chamber to a cap which is part of a rotary assembly that allows the rotation of the said cathode chamber about its axis without twisting the cathode ball connection;

placing the cathode chamber within an anode chamber comprising a second plating solution and an anode;

rotating the cathode chamber on its axis using the rotary assembly;

biasing the said anode with a positive voltage in reference to the said cathode ball causing the electroplating of a metallic coating on the surface of the said powder while it is tumbled within the rotating cathode chamber;

and rinsing, cleaning and optionally ball milling the mixture of the plated powder particles and the spheres to enable easy recovery of the plated powder.

2. A method according to claim 1, wherein the said plating solution is for an electroplating solution.
3. A method according to claim 1, wherein said powder is electrically conducting in the bulk.
4. A method according to claim 1, wherein said powder is nonconducting in the bulk but possesses a surface layer that is electrically conductive.
5. A method according to claim 1, wherein the said electroplating solution is used to produce a thin conductive coating of a low melting point metal or an alloy on said powder.
6. A method according to claim 3, wherein the said powder is selected from the group comprising copper, silver, gold, nickel, palladium, platinum, aluminum or alloys thereof

7. A method according to claim 4, wherein the powder is made of polymeric materials such as teflon, polysulfone, polyimide and provided with a conducting surface layer of copper, silver, nickel, gold, palladium, platinum, aluminum or alloys thereof.
8. A method according to claim 5, wherein said low melting coating is selected from the group comprising indium, tin, bismuth, antimony, lead, zinc or alloys thereof.
9. A method according to claim 1, wherein the cathode chamber is selected from the group comprising polypropylene, polyvinyl chloride, high density polyethylene and Teflon.
10. A method according to claim 1, wherein said anode is selected from the group comprising indium, tin, lead, zinc, bismuth, titanium, platinum or alloys thereof.
11. A method according to claim 1, wherein said permeability of the cathode chamber is achieved using windows made of a microporous polymer film with pore sizes of 1 micrometer or less.
12. A method comprising the step of making an electrically conducting paste by mixing the coated powder from Claim 1 with a suitable polymer resin dissolved in a solvent, butyric acid, and no-clean flux.
13. A method according to claim 12, wherein the said polymer is selected from the group comprising polyimides, polyimide-siloxanes, siloxanes, phenoxy polymers,



styrene allyl alcohol, epoxies, soluble epoxy with a ketal and acetal diepoxides, bio-based resins made from lignin, cellulose, wood oils and crop oils.

14. A method according to claim 12, wherein said solvent is selected from the group consisting of n-methyl pyrrolidione, acetophenone, methyl benzoate, ethyl benzoate, and propylene glycol methyl ether acetate (PGMEA).
15. A method according to claim 12, wherein said paste is disposed between a first and second electrically conductive surface.
16. A method according to claim 15, wherein said first electrically conductive surface is a chip contact location and said second electrically conductive surface is a substrate contact location.
17. A method according to claim 15, wherein said first electrically conducting surface is a liquid crystal display panel contact location and said second electrically conductive surface is a plastic lead location.
18. A method according to claim 12, wherein said paste is heated to a first temperature to fuse said coating on adjacent powder particles and particles to the chip and substrate contact locations.
19. A method according to claim 12, wherein said paste is heated to a second temperature sufficient to cure said polymer.

20. A method according to Claim 12 where the paste is heated to a single temperature to achieve fusing of the said coated powder particles to themselves and to the contact locations and the curing of the said polymer all in one step.

21. A method comprising the steps of:

Precleaning a powder with a conducting surface in a suitable solution to remove surface oxides;

immersing and agitating the clean powder in a electroless immersion plating solution at the appropriate temperature to achieve a deposition of a thin metallic layer on the powder surface;

cleaning and drying the powder;

providing an electrically nonconductive cathode chamber with at least part of its wall area rendered permeable to ions and electrolytic solutions;

premixing a predetermined quantity of a fine electroconductive powder and a first electroplating solution;

filling said cathode chamber with the said powder mixture and a plurality of electroconductive spheres;

disposing an electroconductive cathode ball in contact with said spheres and powder particles;

securing the said cathode chamber to a cap which is part of a rotary assembly that allows the rotation of the said cathode chamber about its axis without twisting the cathode ball connection;

placing the cathode chamber within an anode chamber comprising a second plating solution and an anode;

rotating the cathode chamber on its axis using the rotary assembly;

biasing the said anode with a positive voltage in reference to the said cathode ball causing the electroplating of a metallic coating on the surface of the said powder while it is tumbled within the rotating cathode chamber;

and rinsing, cleaning and optionally ball milling the mixture of the plated powder particles and the spheres to enable easy recovery of the plated powder.

22. A method according to claim 21, wherein the said plating solution is for an electroplating solution.
23. A method according to claim 21, wherein said powder is electrically conducting in the bulk.
24. A method according to claim 21, wherein said powder is nonconducting in the bulk but possesses a surface layer that is electrically conductive.

25. A method according to Claim 21 wherein the first conductive coating applied by electroless immersion plating provides full coverage of the powder surface.
26. A method according to claim 21, wherein the said electroplating solution is used to produce a second thin conductive coating of a low melting point metal or an alloy on said powder.
27. A method according to Claim 21 wherein the said first coating and the said second coating intermix to form lower melting alloys.
28. A method according to claim 23, wherein the said powder is selected from the group comprising copper, silver, gold, nickel, palladium, platinum, aluminum or alloys thereof
29. A method according to claim 24, wherein the powder is made of polymeric materials such as teflon, polysulfone, polyimide and provided with a conducting surface layer of copper, silver, nickel, gold, palladium, platinum, aluminum or alloys thereof.
30. A method according to claim 25, wherein said first conductive coating is selected from the group comprising tin, copper, silver, gold, palladium, nickel or alloys thereof.
31. A method according to Claim 26 wherein the second conductive coating is selected from the group comprising indium, tin, bismuth, antimony, lead, zinc or alloys thereof.

32. A method according to claim 21, wherein the cathode chamber is selected from the group comprising polypropylene, polyvinyl chloride, high density polyethylene and Teflon.
33. A method according to claim 21, wherein said anode is selected from the group comprising indium, tin, lead, zinc, bismuth, titanium, platinum or alloys thereof.
34. A method according to claim 1, wherein said permeability of the cathode chamber is achieved using windows made of a microporous polymer film with pore sizes of 1 micrometer or less.
35. A method comprising the step of making an electrically conducting paste by mixing the coated powder from Claim 21 with a suitable polymer resin dissolved in a solvent, butyric acid, and no-clean flux.
36. A method according to claim 35, wherein the said polymer is selected from the group comprising polyimides, polyimide-siloxanes, siloxanes, phenoxy polymers, styrene allyl alcohol, epoxies, soluble epoxy with a ketal and acetal diepoxides, bio-based resins made from lignin, cellulose, wood oils and crop oils.
37. A method according to claim 35, wherein said solvent is selected from the group consisting of n-methyl pyrrolidone, acetophenone, methyl benzoate, ethyl benzoate, and propylene glycol methyl ether acetate (PGMEA).
38. A method according to claim 35, wherein said paste is disposed between a first and second electrically conductive surface.

39. A method according to claim 38, wherein said first electrically conductive surface is a chip contact location and said second electrically conductive surface is a substrate contact location.
40. A method according to claim 38, wherein said first electrically conducting surface is a liquid crystal display panel contact location and said second electrically conductive surface is a plastic lead location.
41. A method according to claim 35, wherein said paste is heated to a first temperature to fuse said coating on adjacent powder particles and particles to the chip and substrate contact locations.
42. A method according to claim 35, wherein said paste is heated to a second temperature sufficient to cure said polymer.
43. A method according to Claim 35 where the paste is heated to a single temperature to achieve fusing of the said coated powder particles to themselves and to the contact locations and the curing of the said polymer all in one step.

## **An Apparatus and Method for Plating Coatings on to Fine Powder**

### **Materials and Use of the Powder Therefrom**

#### **ABSTRACT OF THE DISCLOSURE**

Methods for forming pastes of powder particles coated with an electrically conductive coating are described. The powder particles, with or without an optional first coating layer applied to their surface separately, are premixed with an electroplating solution and placed in a barrel plater wherein the cathode compartment is a barrel whose walls are in part made of an ion and or electrolyte permeable membrane, along with a charge of conductive and chemically corrosion resistant spheres (e.g., stainless steel balls), a larger cathode ball, and a plating electrolyte (catholyte); the said barrel is immersed in an outer tank which functions as the anode compartment and contains a second plating electrolyte (anolyte) and an anode. The barrel is connected to a motor/gear arrangement to turn it at a controlled rate allowing the powder, the spheres and the cathode to tumble and make contact with one another on a time averaged basis. The cathode is connected to the negative terminal and the anode is connected to the positive terminal of a dc power supply and a dc current is passed through the plating cell with ion/electrolyte flow through the barrel membrane. Using such an apparatus, metal and alloy coatings can be applied to powder materials which are either conducting in their bulk or just on their surface. By proper selection of the membrane, powder down to 2 microns size can be coated which is heretofore not possible to do. The spheres added serve to disperse the powder in the bath and



act as a path to carry current to the powder particles during the plating process. At the end of the plating run, the powder and the spheres are separated from the plating solution, rinsed to remove plating chemicals, and optionally subjected to an attrition milling step to recover the powder from the mixture. Plating of SnBi alloy films on the surface of copper powder in the 5 to 10 micron diameter range has been performed using such an apparatus and method to show the feasibility of this approach. Coated powders produced thus are useful as fillers in electrically and/or thermally conducting adhesive formulations used in microelectronic applications. The powder is added to a polymer material to form a paste which is heated to fuse the powder coating surfaces to form a network of interconnected particles and further heated to cure the polymer. When the paste is disposed between adjacent electrically conductive surfaces, the coated particles fuse to the electrically conductive surface to form electrical interconnections.

**A METHOD OF FABRICATING COATED POWDER MATERIALS AND THEIR**  
**USE FOR**  
**HIGH CONDUCTIVITY PASTE APPLICATIONS**

S. K. Kang, S. Purushothaman, and R. S. Rai

**FIELD OF THE INVENTION**

The present invention is directed to a method of producing metal powders useful in pastes for forming electroconductive connections between electroconductive members, and methods of use of the same in electronic applications.

**BACKGROUND**

Most electrical conductors used in electronic devices are made of metals, such as copper, aluminum, gold, silver, lead/tin (solder), molybdenum and others. Solder connection technology using lead/tin alloys plays a key role in various levels of electronic packaging, such as flip-chip connection (or C4), solder-ball connection in ball-grid-arrays (BGA), and IC package assembly to a printed circuit board (PCB). Solder joints produced in the electronic packages serve critically as electrical interconnections as well as mechanical/physical connections. When either of the functions is not achieved, the solder joint is considered to have failed, which can often threaten a shut-down of the whole electronic system.

When microelectronic packages are assembled to a printed circuit board, the lead-tin eutectic solder, 63%Sn-37%Pb, having the lowest melting point (183 °C) among Pb-Sn alloys, is most widely used. In these applications, there are two solder connection technologies employed for mass production: plated-through-hole (PTH) and surface mount technology (SMT) soldering. The basic difference between the two technologies originates from the difference in the PCB design and its interconnection scheme.

In SMT soldering, microelectronic packages are directly attached to the surface of a PCB. A major advantage of SMT is high packaging density, which is realized by eliminating most PTH's in the PCB as well as by utilizing both surfaces of the PCB to accommodate components. In addition, SMT packages have a finer lead pitch and a smaller package size compared to traditional PTH packages. Hence, SMT has contributed significantly in reducing the size of electronic packages and thereby the volume of the overall system.

In SMT soldering, solder paste is applied to a PCB by screen printing. Solder paste consists of fine solder powder, flux, and organic vehicles. During the reflow process, solder particles are melted, flux is activated, solvent materials are evaporated, and simultaneously molten solder coalesces and is eventually solidified. In contrast, in the wave soldering process, a PCB is first fluxed and components are mounted on it. Then it is moved over a wave of molten solder.

The soldering process is usually completed by subjecting the solder joints to a cleaning step to remove residual flux materials. Due to environmental concerns, CFCs (chlorofluoro carbons) and other harmful cleaning agents used for this purpose are being

eliminated and water-soluble or no-clean flux materials are being used to minimize or eliminate the cleaning steps.

Recent advances in microelectronic devices demand a very fine pitch connection between electronic packages and a printed circuit board (in an order of a few hundred micrometer pitch). The current solder paste technology used in SMT can not handle this very fine pitch interconnection due to the soldering defects such as bridging or solder balling. Another technical limitation of using the Pb-Sn eutectic solder is its high reflow temperature, approximately 215 °C. This temperature is already higher than the glass transition temperature of the epoxy resin used in most polymeric printed circuit board materials. Thermal exposure at this reflow temperature produces significant thermal strains in a printed circuit board after soldering, especially in the direction perpendicular to the surface of a PCB, because no structural reinforcement is made in that direction. Thereby, the residual thermal strains in an assembled PCB could significantly degrade the reliability of an electronic system.

A more serious concern regarding the usage of lead (Pb)-containing solders is an environmental issue, a trend already experienced in other industries and has led to the elimination of lead from gasoline and paints.

In the electronic industry, two different groups of materials are investigated currently for the possibility of substituting the Pb-containing solder materials; Pb-free solder alloys, and electrically conductive pastes (ECP). The present invention discusses the development and applications of the electrically conductive paste materials. An electrically conductive paste (or adhesive) is made of metallic filler particles loaded in the matrix of a polymer material. The polymer matrix can be any polymer suitable for use

in a paste, for example, a thermoplastic or thermoset. The polymer is selected preferably from the group comprising epoxy, polyester and polyimide. The soluble epoxy, in particular, soluble ketal and acetal diepoxides, as described in U.S. application serial no. 08/210,879, the teaching of which is incorporated herein by reference can also be used as the polymer matrix. Referring to Fig. 1, silver-particle 2 filled epoxy 4 is the most common example of the electrically conductive pastes 6, schematically shown therein as disposed between surface 8 and surface 10. The silver particles usually in the shape of flakes provide electrical conduction by percolation mechanism, while the epoxy matrix provides adhesive bond between the components and a substrate. This silver-filled epoxy material has been long used in the electronic applications as a die-bonding material, where its good thermal conduction rather than electrical conduction property is utilized. However, this material has not been accepted for the applications requiring high electroconduction and fine pitch connection. The silver-filled epoxy material has several limitations, such as low electrical conductivity, increase in contact resistance during thermal exposure, low joint strength, silver migration, difficulty in rework, and others. Since this silver-filled epoxy material is electrically conductive in all the directions, it is classified as "isotropic" in electro-conduction. There is another class of electrically conductive adhesive (or film), which provides electroconduction only in one direction. This class of the materials is known as "anisotropic" conductive adhesive film 12, shown schematically in FIG. 2A, which contains electrically conductive particles 14 in a binder or adhesive material 16. The anisotropic conductive adhesive or film 12 becomes conductive only when it is compressed between two conducting surfaces 18 and 20 as shown in FIG. 2B. This process normally requires heat and pressure. The major application of the anisotropic conductive film is for joining of a liquid crystal display panel to its electronic printed circuit board. The conducting particles 14 are usually deformable, such as solder balls,

or plastic balls coated with nickel and gold. The binder or adhesive material 16 is mostly a thermosetting resin.

The ECP made of Sn-plated Cu powder and polyimide-siloxane resin disclosed in our earlier patent application, YO994-097, is a good candidate for the high temperature solder joints such as controlled collapse chip connections (C4) and solder ball connection (SBC) to a ceramic substrate. However, for the polymeric printed circuit board applications, this ECP is not adequate, because the reflow temperature such as 250 °C is much higher than the glass transition temperature of the polymeric resin, for example, FR-4. Candidates for this purpose are ECP's made of Cu powder plated with Indium, tin-bismuth alloys or Indium-tin alloys, formulated with polyimide-siloxane resin. The reflow temperature of these powder pastes is expected to be between 120 and 180 °C, which is even lower than the reflow temperature of the Pb/Sn eutectic solder, 215 °C.

In an earlier patent application YO994281 dated March 31, 1995, we have disclosed a process to produce dendritic copper powder overcoated with Sn or Sn and BiSn coatings by electrolytic plating on a rigid inert cathode. The morphology of the powder that can be made by this technique is restricted to the dendritic shape which is not always the preferred one for all ECP applications.

A solder/polymer composite paste material is disclosed in U. S. Pat. No.5,062,896 (Huang et. al.), comprising a major proportion of a meltable solder powder filler, such as Bi-Sn, Pb-Sn, Bi-Sn-Pb alloys, a minor proportion of a thermoplastic polymer such as a polyimide siloxane, and a minor proportion of a fluxing agent. An oxide-free, partially coalesced solder alloy connection is obtained, which is polymer strengthened

and reworkable at a low reflow temperature, per se, or in the presence of polymer solvent.

In U. S. Pat. No.5,286,417 (Mahmoud et. al.), a fusible conductive adhesive is disclosed, which comprises metal alloy fillers such as Sn-Au and Bi-Au, and a thermoplastic polymer having a glass transition temperature overlapping the melting temperature of the metal filler alloys. The loading of the conductive material in the polymer is in the range of about 15% to about 20% by weight.

In U. S. Pat. No.5,136,365 (Pennisi et. al.), an adhesive material is disclosed, which contains a fluxing agent and metal particles for use in reflow soldering such as Sn, Pb, In, Bi, Sb, Ag and others, in the matrix of an epoxy resin. Upon reflow soldering, the said adhesive forms anisotropic electroconduction between an electrical component and a substrate.

In U. S. Pat. No.5,213,715 (Patterson et. al.), a directionally conductive polymer is disclosed, which contains a metallic filler powder of Ni or Cu. The metallic powder is treated by a different polymer than the polymer used as a matrix resin. Upon compression, the coated polymer dissolves to make an electrical conduction among the filler particles.

### OBJECTS

It is an object of the present invention to coat free standing metallic powder of any desired shape, morphology and size with a surface coating of a metal or an alloy by electroplating.



It is another object of the present invention to provide a method of fabricating an electrically conductive paste material which is environmentally safe and low cost.

It is another object of the present invention to provide a method of fabricating an electrically conductive paste material which produces a higher electrical conductivity than the conventional silver-filled epoxy does.

It is another object of the present invention to provide a method of fabricating an electrically conductive paste material which can be processed at a lower temperature than the reflow temperature of Pb-Sn eutectic solder paste.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Further objects, features, and advantages of the present invention will become apparent from a consideration of the following detailed description of the invention when read in conjunction with the drawing FIGs., in which:

FIG. 1 is a schematic illustration of an electrically conductive paste comprising silver flake particles as a filler in the matrix of epoxy resin. The conductive paste is classified as isotropic in electroconduction.

FIG. 2 is a schematic illustration of an electrically conductive adhesive which becomes electrically conductive only in the one direction when the adhesive film is compressed between two contact or bond pads. The conductive adhesive (or film) is classified as anisotropic.

FIG. 3 is a schematic illustration of an electrically conductive paste material, comprising spherical copper powder filled in the matrix of thermoplastic polymer resin. The copper particles are coated with a low melting point, non-toxic metal such as tin, indium, bismuth, antimony or combinations thereof.

FIG. 4 is a schematic illustration of the apparatus used to electrolytically deposit thin metal or alloy coatings on fine copper powder.

FIG. 5 is a SEM (scanning electron micrograph) of the structure of SnBi alloy coated copper powder made using the apparatus in Fig. 4 and using the process described below.

FIG. 6 is a scanning electron micrograph of copper powder coated first with electroless Sn followed by a SnBi alloy coating showing its shape and morphology.

FIG. 7 is a differential scanning calorimeter (DSC) scan of the SnBi plated copper powder showing the three distinct melting processes that occur in the coating layer.

FIG. 8 is an x-ray diffractogram of the SnBi plated copper powder showing the presence of peaks characteristic of crystalline copper, tin and bismuth.

FIG. 9 is a DSC scan of the Sn and then SnBi coated copper powder showing a single distinct melting point of the coating layer at 140 C. Note the broad melting at temperatures above 140 C.

FIG 10 is re-scan of the sample scanned once as in FIG. 9. Note that the scan shows a larger peak at 140 C and the absence of the broad melting at higher temperatures.

### SUMMARY OF THE INVENTION

A broad aspect of the present invention is a method including the steps of disposing a powder with a conducting surface in a plating solution contained in a plating cell and allowing it to be in contact with the cathode of the cell; disposing and immersing an anode covered with an optional membrane that is permeable to the plating solution but not the powder particles; providing a controlled agitation to the cell such that the powder bed on the cathode is continuously turned over allowing different powder particles to be in direct contact with the cathode; applying an electrical potential across the anode and cathode to set up current flow through the electrolyte and facilitate electrolytic plating of the desired coating from the solution on to the powder particles.

A second aspect of the present invention is to produce a powder with two or more layers applied by successive combinations of electroless plating and electroplating as described in the preceding paragraph to achieve a more versatile combination of coating properties.

In a more particular aspect of this invention, the coated powder separated from the solution, rinsed and dried and used to formulate electrically conducting adhesives by mixing with a polymer resin dissolved in a suitable solvent.

### DETAILED DESCRIPTION

According to an embodiment of the present invention, an electrically conductive paste (ECP) material is disclosed, which consists of copper powder coated with a thin layer of low melting point, Pb-free metals selected from Sn, In, Bi, Sb and their alloys, mixed with an environmentally-safe fluxing agent, and dispersed in the matrix of thermoplastic or thermosetting polymers. The microstructure of the ECP containing SnBi coated Cu powder is shown schematically in a cross-section view in FIG. 3.

In one particular embodiment, we disclose a new electrically conductive paste material consisting of copper powder coated with a tin bismuth alloy, polyimide-siloxane, solvent (acetophenone or n-methyl pyrrolidone) and a carboxylic acid/surfactant. The tin/bismuth coated copper powder is produced by simultaneous electrodeposition of tin and bismuth atoms as an alloy from a commercial electroplating solution produced by Lea Ronal Corporation using the special apparatus illustrated in Fig. 4.

The apparatus consists of an external container 1 made of a nonconducting material, preferably a plastic such as polypropylene or high density polyethylene. A cathode sub-chamber 2 made of stainless steel is mounted within this container as shown in Fig. 4 at the bottom. The shape of this cathode chamber is essentially cylindrical except the inside bottom surface has been milled to a shallow curvature to provide a curved rather than a flat bottom. The cathode is provided with an extension 3 that allows external electrical connection to be made to this member. Appropriate o-ring seals 4 are provided to ensure that this extension will not cause any leakage of fluids from the container. The cathode is covered with plater's tape or an insulating lacquer 5 at all inside surfaces except at the inside bottom and about 5mm height on the inside sidewall. The uncoated area is the active cathode surface of the cell.

A preweighed amount of conductive powder 6, to be coated is placed in the cathode chamber and the container is filled with a suitable electroplating solution 7 (in this case a SnBi plating solution) so as to partially fill the cathode sub-chamber. The cap 8 of the container 1 is fitted with a suitable anode 9, in the present case a bar of pure tin, and is provided with a means 10 to make electrical connection. An optional membrane 11 is wrapped around and secured on the anode. This membrane is a liquid and ion permeable polymer membrane, for example Daramic made by W.R. Grace and Company and commonly employed as separator in lithium ion batteries with liquid or gel electrolytes. This serves to allow ion and liquid transport and exchange between the anode and the cathode through its micron sized porosity, while preventing any physical contact between the particles and the anode. Thus it eliminates the possibility of electrolytic dissolution of the powder or any coatings thereon due to contact with the anode 9 which is held at a positive electrical potential. The length and diameter of the anode is such that it fits within the cathode sub-chamber and its bottom surface is about 6 mm from the bottom inner surface of the cathode sub-chamber. The lid 9 is secured tightly such that any agitation of the assembly does not lead to leaking of the electroplating solution from the container.

The anodes and cathode leads 10 and 3 are connected to the positive and the negative legs, respectively, of a dc power supply (for example Kepco Model JQE 0 to 6V/ 0 to 20 Amps). The closed container is mounted on a shaker stand (for example Mistral Multimixer made by Lab Line Instruments, Illinois) which allows controlled lateral shaking of the container's contents. This motion is used to facilitate turning over the bed of powder 6 on the bottom inner surface of the cathode sub-chamber 2 so that different powder particles will be brought in direct contact with that surface over time. A dc voltage is applied to the cell to achieve a plating current through the cell. As the particles tumble on and off the cathode surface they are plated when they are in contact

with the cathode. Different particles get plated randomly at different instances of time during this agitation leading to coverage of the particles. The plating conditions (namely the voltage, current), the agitation level, and the plating time are variables that are experimentally varied to identify optimum conditions that yield the best results in terms of coverage of the powder and the composition of the coating (as this latter property depends on the local current density in the vicinity of the surface being plated). Figure 5 is an SEM photograph of copper powder electroplated with SnBi alloy using this apparatus.

The copper powder may be substituted with others such as nickel, cobalt, silver, palladium, platinum depending on the specific application. Alternatively, one can also use powder that is nonconducting in the bulk but provided with an electrically conductive surface layer. Metallized ceramic or polymer powder is a typical example of this class of materials. The tin/bismuth alloy coating can be replaced by other metals such as Sn, In, Zn, Pb, Bi and Sb or their alloys. Because the process can start with any powder size or aspect ratio, a wide variety of coated filler powders can be prepared.

When such a powder is formulated into an ECP, a joining operation can be performed near the melting point of Sn/Bi alloy which is about 140°C resulting in sound metallurgical bonding between the particles themselves and between the particles and substrate contact pad surfaces on electronic devices and cards which are typically made of copper, copper/gold, nickel, nickel/gold, nickel/palladium, palladium, or palladium/gold.

Alternately, a coating of indium (melting point 159°C) or an alloy of indium and tin (melting point 120 °C) can be used as coatings on the copper particles to obtain bonding as described above. Since indium alloys have acceptable wettability on even hard to



solder metals such as aluminum, titanium, molybdenum, or tungsten, the present invention material can be used as fillers in ECP's for joining of liquid crystal display devices. The joining process can be either solid-state or liquid-solid reaction. The polymer curing process can be combined with the joining process depending on the paste formulation so that both these can be achieved in a single bonding cycle. Because of the metallurgical bonding and the high conductivity copper core, a higher electrical conductivity is expected with the joints made of the new paste material than with those of the silver-epoxy material. The metallurgical bonds also provide stable electrical conductivity of the new joints upon thermal exposure and cycling. It is also expected to have a higher joint strength from the combined effect of the metallurgical and adhesive bonds. It should be noted that such bonding is achieved at significantly lower temperatures than what is currently practiced for PbSn eutectic solder assemblies (215°C) thereby reducing the thermal stresses and the associated warpage that may occur in card substrates.

In another variant of the coating composition a low melting temperature and uniform coverage can be achieved in the following manner. A coating of a thin layer of Sn can be applied by electroless plating first on the copper powder as described in our earlier application, YO994-097. This is followed by electroplating the SnBi alloy as described in the present invention. The combination would ensure complete coverage of all copper surfaces and provide a low melting coating alloy. Figure 6 is an SEM photograph of copper powder first plated with Sn by an electroless process and then electroplated with SnBi by the process described herein. In a more general variant, the coating can be any metal or alloy that can be coated on the powder by an electroless or electrolytic plating, with additional coating of metal or alloy that can be applied by electrolytic or electroless plating with the combination providing the desired lower melting point alloy.



The polymer component of the paste can be polymer resins prepared from renewable resources or bio-based materials after appropriate functionalization to achieve the desirable thermal and rheological properties. Lignin (by product from paper manufacture), cellulose, wood or crop oils are potential candidates for this purpose. Use of these materials is environmentally preferable because they are derived from natural and renewable resources and can be disposed of more readily at the end of the useful life of the electronic assembly. This is particularly attractive because the use of the coated copper powder as filler eliminates the use of lead (Pb) containing solders and the resulting paste formulation is non-toxic and easy to dispose.

Our previous application, Serial #326,626 filed on October 24, 1994, the teaching of which is incorporated herein by reference teaches using tin-coated copper powder as a filler material in formulating an electrically conductive paste. The copper powder has a spherical morphology, which can be produced by either powder atomization or electrodeposition process. Tin coating is performed on copper powder by using an electroless immersion Sn plating solution.

Since there is no commercial immersion plating process available for many of the coating metals of interest, specifically indium, bismuth and antimony, coating of copper powder by a process similar to tin-coating on copper powder described above is not possible.

The process and structure of the present invention provides the solution to the above problems through an electroplating method to coat In, Bi, Sb, Sn and Pb or alloys

thereof on free standing powder particles. The method is also applicable to other metal coatings that cannot be obtained easily by electroless plating.

### **Example 1**

About 1 gm of spheroidal copper powder nominally 5 to 7 micron diameter supplied by Degussa Corporation, South Plainfield, NJ, was cleaned in a 5% sulfuric acid/water solution to remove the native surface oxide, rinsed in deionized water and then isopropanol and dried. The cathode barrel of the plating setup was assembled on to the containment vessel and then filled with 30 ml of the SnBi alloy plating solution purchased from LeaRonan Corporation. The cleaned copper powder was transferred and stirred into a suspension in the solution. The top cap of the containment vessel was screwed on resulting in the Sn anode being immersed in the plating solution contained in the cathode barrel. The assembly was then placed on the shaker apparatus (Mistral Multimixer made by Labline Instruments, Illinois) and secured to the vibrating top platform. The anode of the plating cell was connected to the positive terminal and the cathode was connected to the negative terminal of a Kepco JQE 0 to 6V/ 0 to 20 Amps dc power supply. The shaker was set to oscillation level 5. The dc power supply was turned on and a plating current of 2 amps was established at a supply voltage of about 2 to 4 volts. Plating was carried out for 10 minutes. The power supply was turned off, the leads disconnected, and the plating cell disassembled. The used plating solution was pipetted out, the powder rinsed thoroughly in deionized water and isopropanol to eliminate any residual plating chemicals. The powder was then scooped out of the barrel, dried and pulverized with a pestle and mortar if necessary. Figure 6 is a scanning electron microscope (SEM) photograph of the plated powder particles.

A small sample of the powder (usually 10 mg) was loaded into a Model SSC/5200 differential scanning calorimeter (DSC) made by Seiko Inc.. The sample was heated at a rate of 5 degrees C per minute from room temperature to 300C to monitor the melting processes that occur in the material. Fig. 7 shows a typical DSC scan indicating that distinct melting processes occur at 140 C, 200 C and 270 C corresponding to the melting of a eutectic SnBi alloy, a off-eutectic bismuth rich SnBi alloy that melts at 200 C and the melting of some free bismuth, respectively. It is important to note that the surface coating has an incipient melting point of 140 C.

A small amount of the plated powder was sprinkled on a glass slide with a double stick adhesive tape on it, to make a thin bed of powder. The sample was then loaded in to a Philips X-ray diffractometer and a  $\theta/2\theta$  x-ray diffraction scan was performed to identify characteristic peaks of the crystalline phases in the powder. A typical scan shown in Figure 8, indicates that diffraction peaks corresponding to Cu, Sn and Bi are present and the copper coverage by the SnBi coating is good. Thus it was concluded that the above described procedure produces fine copper powder overcoated with a SnBi alloy layer with a lowest melting point of 140 C.

### **Example 2**

A small amount of spheroidal copper powder nominally 5 to 7 micron diameter supplied by Degussa Corporation, South Plainfield, NJ, was cleaned in a 5% sulfuric acid/water solution to remove the native surface oxide, rinsed in deionized water and then isopropanol. Clean copper powder was transferred into an immersion tin plating solution, TINPOSIT LT-34, from Shipley, Marlboro, MA. to produce a thickness of 0.3 to 0.5  $\mu\text{m}$  on 5-7  $\mu\text{m}$  copper powder.

The cathode barrel of the plating setup was assembled on to the containment vessel and then filled with 30 ml of the SnBi plating solution, SOLDERON BI, purchased from LeaRonai Corporation, Freeport, NY. The Sn coated copper powder was transferred and stirred into a suspension in the solution. The top cap of the containment vessel was screwed on resulting in the Sn anode being immersed in the plating solution contained in the cathode barrel. The assembly was then placed on the shaker apparatus (Mistral Multimixer made by Labline Instruments, Illinois) and secured to the vibrating platform. The anode of the plating cell was connected to the positive terminal and the cathode was connected to the negative terminal of a Kepco JQE 0 to 6V / 0 to 20 amps dc power supply. The shaker was set to oscillation level 5. The dc power supply was turned on and a plating current of 2 amps was established at a supply voltage of about 2 to 4 volts. Plating was carried out for 10 minutes. The power supply was turned off, the leads disconnected, and the plating cell disassembled. The used plating solution was pipetted out, the powder rinsed thoroughly in deionized water and isopropanol to eliminate any residual plating chemicals. The powder was then scooped out of the barrel, dried and pulverized with a pestle and mortar if necessary.

A small sample of the powder (usually 10 mg) was loaded into a Model SSC/5200 differential scanning calorimeter (DSC) made by Seiko Inc.. The sample was heated at a rate of 5 degrees C per minute from room temperature to 300C to monitor the melting processes that occur in the material. Fig. 9 shows a typical DSC scan indicating a single distinct melting process at 140 C corresponding to the melting of a eutectic SnBi alloy with a broad melting behavior seen at higher temperatures without any distinct peaks. It is important to note that this is in contrast to the multiple melting point behavior seen in Example 1. This is believed to be a result of the combination of the excess Bi and the

Bi rich alloy in the electroplated SnBi coating with the electroless plated Sn undercoat to form a near-eutectic mixture. A second DSC scan of the powder already scanned to 300 C once , Figure 10, confirms this since it only exhibits a single and larger melting peak at 140 C.

A small amount of the plated powder was sprinkled on a glass slide with a double stick adhesive tape on it, to make a thin bed of powder. The sample was then loaded in to a Philips X-ray diffractometer and a  $\theta/2\theta$  x-ray diffraction scan was performed to identify characteristic peaks of the crystalline phases in the powder. A typical scan shown in Figure 11, indicates that diffraction peaks corresponding to Cu, Sn and Bi are present and the copper coverage by the SnBi coating is good. Comparison with Figure 8 shows that the copper coverage by the coating is more complete as would be expected from the process used in Example 2.

Thus it was concluded that the above described procedure produces fine copper powder overcoated with a eutectic SnBi alloy layer with a single melting point of 140 C.

### Example 3

The BiSn-plated copper powder was used to formulate a conducting paste by mixing with polyimide siloxane resin dissolved in a solvent of NMP, acetophenone, or ethyl benzoate, and a no-clean flux, FLUX305, from Qualitek International, Inc., Addison, IL. The relative amount of the filler powder over the polymer resin varied from 30 to 90% in weight, depending on a specific application. To insure uniform dispersion of the ingredients, the mixture was processed in a three-roll shear mill. When the filler weight

percent is low, a solvent drying process, for example, 100 °C, 1 h, is required to adjust the viscosity of the paste before dispensing the paste on to a desired foot print.

In order to characterize the electrical and mechanical properties, model joint samples made of the BiSn-plated filler conductive paste were manufactured by laminating two "L-shaped" copper coupons. The lamination was performed at a temperature slightly above the melting point of BiSn coating, for example, 180 °C, at a pressure of 25 psi. Contact resistance of the model joints were measured by four point probe method. The contact resistance values from a nominal joint area of 1.25 mm in diameter ranged from 1.4 to  $4.0 \times 10^{-4} \Omega$ . These values were equivalent to those of the model joints made with a commercial Ag-filled conductive paste.

The shear strength of the model joints made of the BiSn-plated powder was in the range of 5.7 to 8.2 lb, which was comparable to or better than those of the commercial paste.

#### **Example 4**

The powder obtained in Example 2, Sn- and BiSn-plated copper powder (Cu/Sn/BiSn), was used to formulate a conducting paste by mixing with polyimide siloxane resin dissolved in a solvent of NMP, acetophenone, or ethyl benzoate, and a no-clean flux, FLUX305, from Qualitek International, Inc., Addison, IL. The relative amount of the filler powder over the polymer resin varied from 30 to 90% in weight, depending on a specific application.

In order to characterize the electrical and mechanical properties, model joint samples made of the BiSn-plated filler conductive paste were manufactured by laminating two "L-shaped" copper coupons. The lamination was performed at a temperature slightly above the melting point of BiSn coating, for example, 180 °C, at a pressure of 25 psi.

Both electrical and mechanical properties of the model joint samples were characterized by four-point probe and shear testing. The contact resistance from the nominal joint area of 1.25 mm in diameter ranged from 1.3 to  $2.5 \times 10^{-4} \Omega$ . These values were equivalent to those of the model joints made with a commercial Ag-filled conductive paste. The shear strength of the model joints was in the range of 6.5 to 8.9 lb, which was better than those of the commercial paste.

While the present invention has been described with respect to preferred embodiments, numerous modifications, changes, and improvements will occur to those skilled in the art without departing from the spirit and scope of the invention.



## CLAIMS

What is claimed is:

1. A method comprising the steps of:

providing a hollow cathode container filled with a suitable plating solution;

securing the said hollow cathode chamber within a second containment chamber;

disposing a mass of powder with a conducting surface within and at the bottom of the cathode chamber in contact with said electroplating solution;

disposing a conducting anode covered with an ion permeable but electrically nonconducting membrane within this cathode chamber;

providing a means to agitate and tumble the said powder on the said bottom inner surface of the cathode chamber;

and biasing the said anode with a positive voltage in reference to the said cathode chamber causing the electroplating of a metallic coating on the surface of the said powder.

2. A method according to claim 1, wherein the said plating solution is for an electroplating solution.
3. A method according to claim 1, wherein said powder is electrically conducting in the bulk.
4. A method according to claim 1, wherein said powder is nonconducting in the bulk but possesses a surface layer that is electrically conductive.
5. A method according to claim 1, wherein the said electroplating solution is used to produce a thin conductive coating of a low melting point metal or an alloy on said powder.
6. A method according to claim 3, wherein the said powder is selected from the group comprising copper, silver, gold, nickel, palladium, platinum, aluminum or alloys thereof
7. A method according to claim 4, wherein the powder is made of polymeric materials such as teflon, polysulfone, polyimide and provided with a conducting surface layer of copper, silver, nickel, gold, palladium, platinum, aluminum or alloys thereof.
8. A method according to claim 5, wherein said low melting coating is selected from the group comprising indium, tin, bismuth, antimony, lead, zinc or alloys thereof.

9. A method according to claim 1, wherein the cathode chamber is selected from the group comprising aluminum, titanium, and stainless steel.
10. A method according to claim 1, wherein said anode is selected from the group comprising indium, tin, lead, zinc, bismuth, titanium, platinum or alloys thereof.
11. A method according to claim 1, wherein said ion-permeable membrane is made of a microporous polymer film with pore sizes of 1 micrometer or less.
12. A method comprising the step of making an electrically conducting paste by mixing the coated powder from Claim 1 with a suitable polymer resin dissolved in a solvent, butyric acid, and no-clean flux.
13. A method according to claim 12, wherein the said polymer is selected from the group comprising polyimides, polyimide-siloxanes, siloxanes, epoxies, soluble epoxy with a ketal and acetal diepoxides, bio-based resins made from lignin, cellulose, wood oils and crop oils.
14. A method according to claim 12, wherein said solvent is selected from the group consisting of n-methyl pyrrolidione, acetophenone, methyl benzoate and ethyl benzoate.
15. A method according to claim 12, wherein said paste is disposed between a first and second electrically conductive surface.

16. A method according to claim 15, wherein said first electrically conductive surface is a chip contact location and said second electrically conductive surface is a substrate contact location.
17. A method according to claim 15, wherein said first electrically conducting surface is a liquid crystal display panel contact location and said second electrically conductive surface is a plastic lead location.
18. A method according to claim 12, wherein said paste is heated to a first temperature to fuse said coating on adjacent powder particles and particles to the chip and substrate contact locations.
19. A method according to claim 12, wherein said paste is heated to a second temperature sufficient to cure said polymer.
20. A method according to Claim 12 where the paste is heated to a single temperature to achieve fusing of the said coated powder particles to themselves and to the contact locations and the curing of the said polymer all in one step.
21. A method comprising the steps of:

Precleaning a powder with a conducting surface in a suitable solution to remove surface oxides;

immersing and agitating the clean powder in a electroless immersion plating solution at the appropriate temperature to achieve a deposition of a thin metallic layer on the powder surface;

cleaning and drying the powder;

providing a hollow cathode chamber filled with a suitable plating solution;

placing the said hollow cathode chamber within a second containment chamber;

disposing a mass of coated powder from above within and at the bottom of the cathode chamber in contact with said electroplating solution;

disposing a conducting anode covered with an ion permeable but electrically nonconducting membrane within this cathode chamber;

providing a means to agitate and tumble the said powder on the said bottom inner surface of the cathode chamber;

and biasing the said anode with a positive voltage in reference to the said cathode chamber causing the electroplating of a second metallic coating on the surface of the said powder.

22. A method according to claim 21, wherein the said plating solution is for an electroplating solution.

23. A method according to claim 21, wherein said powder is electrically conducting in the bulk.
24. A method according to claim 21, wherein said powder is nonconducting in the bulk but possesses a surface layer that is electrically conductive.
25. A method according to Claim 21 wherein the first conductive coating applied by electroless immersion plating provides full coverage of the powder surface.
26. A method according to claim 21, wherein the said electroplating solution is used to produce a second thin conductive coating of a low melting point metal or an alloy on said powder.
27. A method according to Claim 21 wherein the said first coating and the said second coating intermix to form lower melting alloys.
28. A method according to claim 23, wherein the said powder is selected from the group comprising copper, silver, gold, nickel, palladium, platinum, aluminum or alloys thereof
29. A method according to claim 24, wherein the powder is made of polymeric materials such as teflon, polysulfone, polyimide and provided with a conducting surface layer of copper, silver, nickel, gold, palladium, platinum, aluminum or alloys thereof.

30. A method according to claim 25, wherein said first conductive coating is selected from the group comprising tin, copper, silver, gold, palladium, nickel or alloys thereof.
31. A method according to Claim 26 wherein the second conductive coating is selected from the group comprising indium, tin, bismuth, antimony, lead, zinc or alloys thereof.
32. A method according to claim 21, wherein the cathode chamber is selected from the group comprising aluminum, titanium, and stainless steel.
33. A method according to claim 21, wherein said anode is selected from the group comprising indium, tin, lead, zinc, bismuth, titanium, platinum or alloys thereof.
34. A method according to claim 21, wherein said ion-permeable membrane is made of a microporous polymer film with pore sizes of 1 micrometer or less.
35. A method comprising the step of making an electrically conducting paste by mixing the coated powder from Claim 21 with a suitable polymer resin dissolved in a solvent, butyric acid, and no-clean flux.
36. A method according to claim 35, wherein the said polymer is selected from the group comprising polyimides, polyimide-siloxanes, siloxanes, epoxies, soluble epoxy with a ketal and acetal diepoxides, bio-based resins made from lignin, cellulose, wood oils and crop oils.



37. A method according to claim 35, wherein said solvent is selected from the group consisting of n-methyl pyrrolidione, acetophenone, methyl benzoate and ethyl benzoate.
38. A method according to claim 35, wherein said paste is disposed between a first and second electrically conductive surface.
39. A method according to claim 38, wherein said first electrically conductive surface is a chip contact location and said second electrically conductive surface is a substrate contact location.
40. A method according to claim 38, wherein said first electrically conducting surface is a liquid crystal display panel contact location and said second electrically conductive surface is a plastic lead location.
41. A method according to claim 35, wherein said paste is heated to a first temperature to fuse said coating on adjacent powder particles and particles to the chip and substrate contact locations.
42. A method according to claim 35, wherein said paste is heated to a second temperature sufficient to cure said polymer.
43. A method according to Claim 35 where the paste is heated to a single temperature to achieve fusing of the said coated powder particles to themselves and to the contact locations and the curing of the said polymer all in one step.

# **A METHOD OF FABRICATING COATED POWDER MATERIALS FOR HIGH CONDUCTIVITY PASTE APPLICATIONS**

## **ABSTRACT OF THE DISCLOSURE**

Methods for forming pastes of powder particles coated with an electrically conductive coating are described. The powder particles, with or without an optional first coating layer applied to their surface separately, are placed in contact with a cathode surface immersed in an electroplating solution. An anode covered with a nonconducting but ion-permeable membrane is immersed in the solution in close proximity to the cathode. Agitation to move and gently tumble the powder over the cathode surface is provided. The powder particles are plated with a metallic or alloy coating by biasing the anode with a positive voltage relative to the cathode. The coated powder is removed, rinsed and dried. The powder is added to a polymer material to form a paste which is heated to fuse the powder coating surfaces to form a network of interconnected particles and further heated to cure the polymer. When the paste is disposed between adjacent electrically conductive surfaces, the coated particles fuse to the electrically conductive surface to form electrical interconnections.

Fig. 1

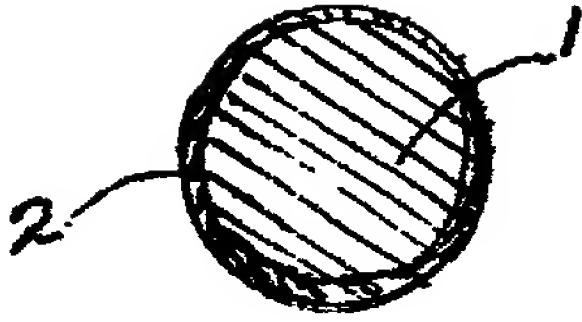


Fig. 2

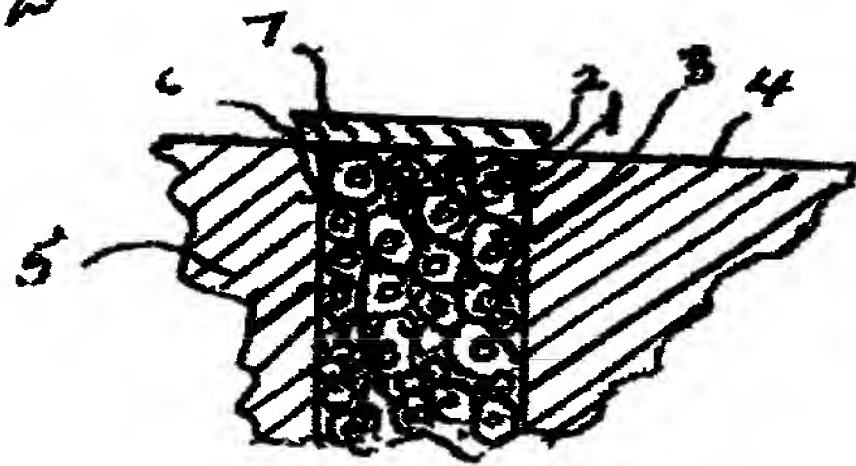


Fig. 3

Paste ID	Filler (wt%)	Resin (%)	Reflow condition	Electrical (mean/st'd)	Mechanical (mean/st'd)	Remark
AgCu01	Ag & Cu (>93)	epoxy	150C, 25psi 30 min	0.00040 (0.00002)	4.3(0.9)	commercial paste
				<b>IN OHMS</b>	<b>IN LBS</b>	
BiSn48	BiSn/Cu (68)	epxy(86) phxy(10) flux(4)	188C, 50 psi 30 min	0.00041 (0.00006)	6.7(0.5)	medium flow resin
BiSn49	BiSn/Cu (76)	epxy(43) lim-ox(43) phxy(10) flux(4)	188C, 25psi 30 min	0.00027 (0.00004)	5.4(0.9)	high flow resin
BiSn53	BiSn/Cu (77)	epxy(43) lim-ox(43) phxy(10) flux(4)	188C, 25psi 30 min	0.00023 (0.00003)	5.1(0.3)	high flow resin
BiSn54	BiSn/Cu (81)	lim-ox(88) epxy(4) phxy(4) flux(4)	188C, 25psi 30 min	0.00018 (0.00002)	3.4(0.3)	very high flow resin

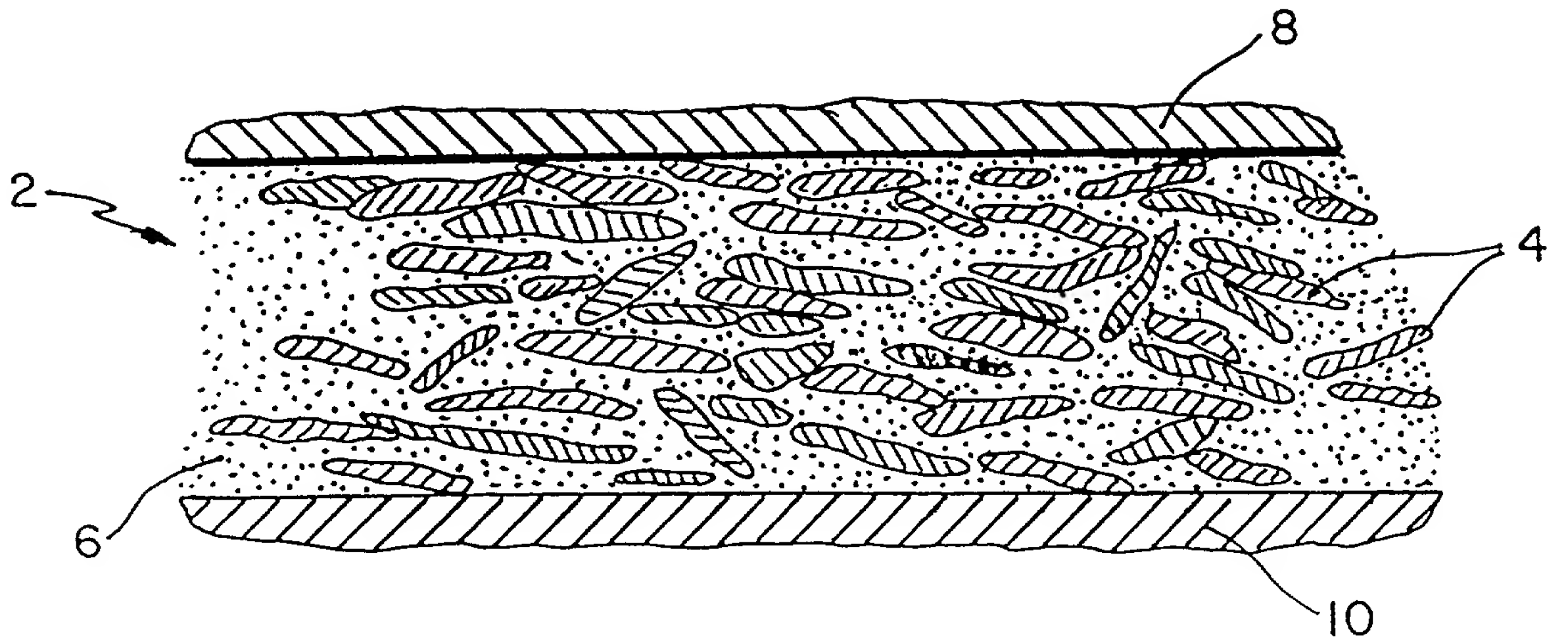


FIG. 1

FIG. 2A

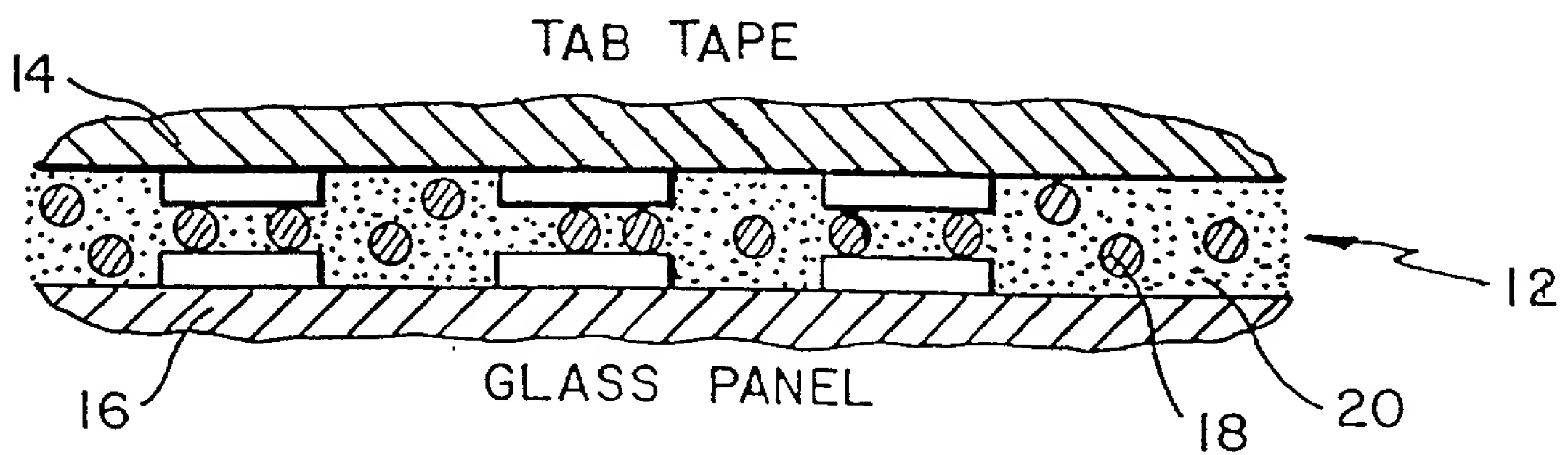
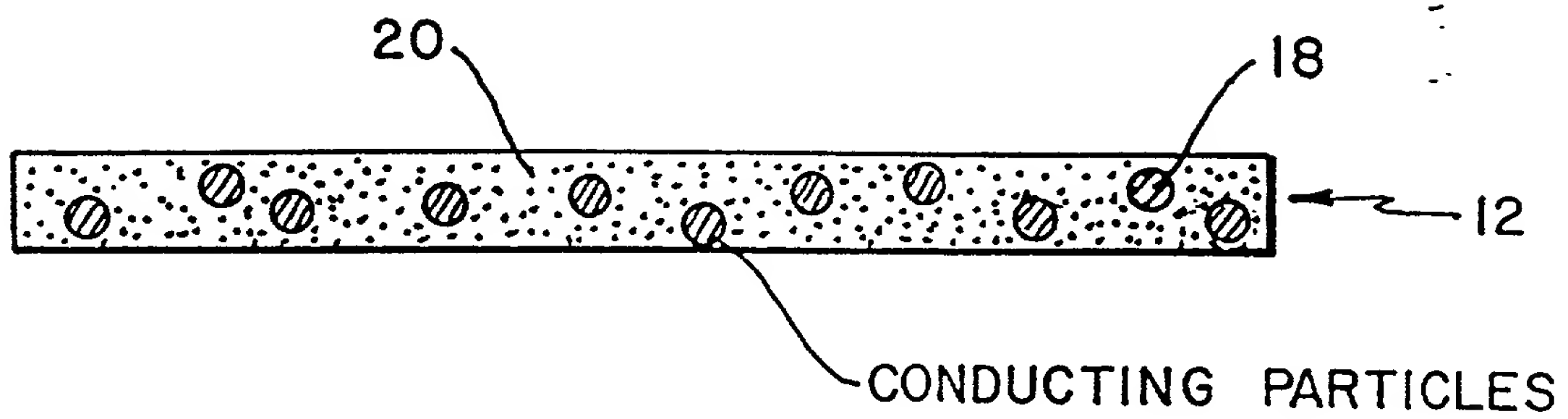


FIG. 2B

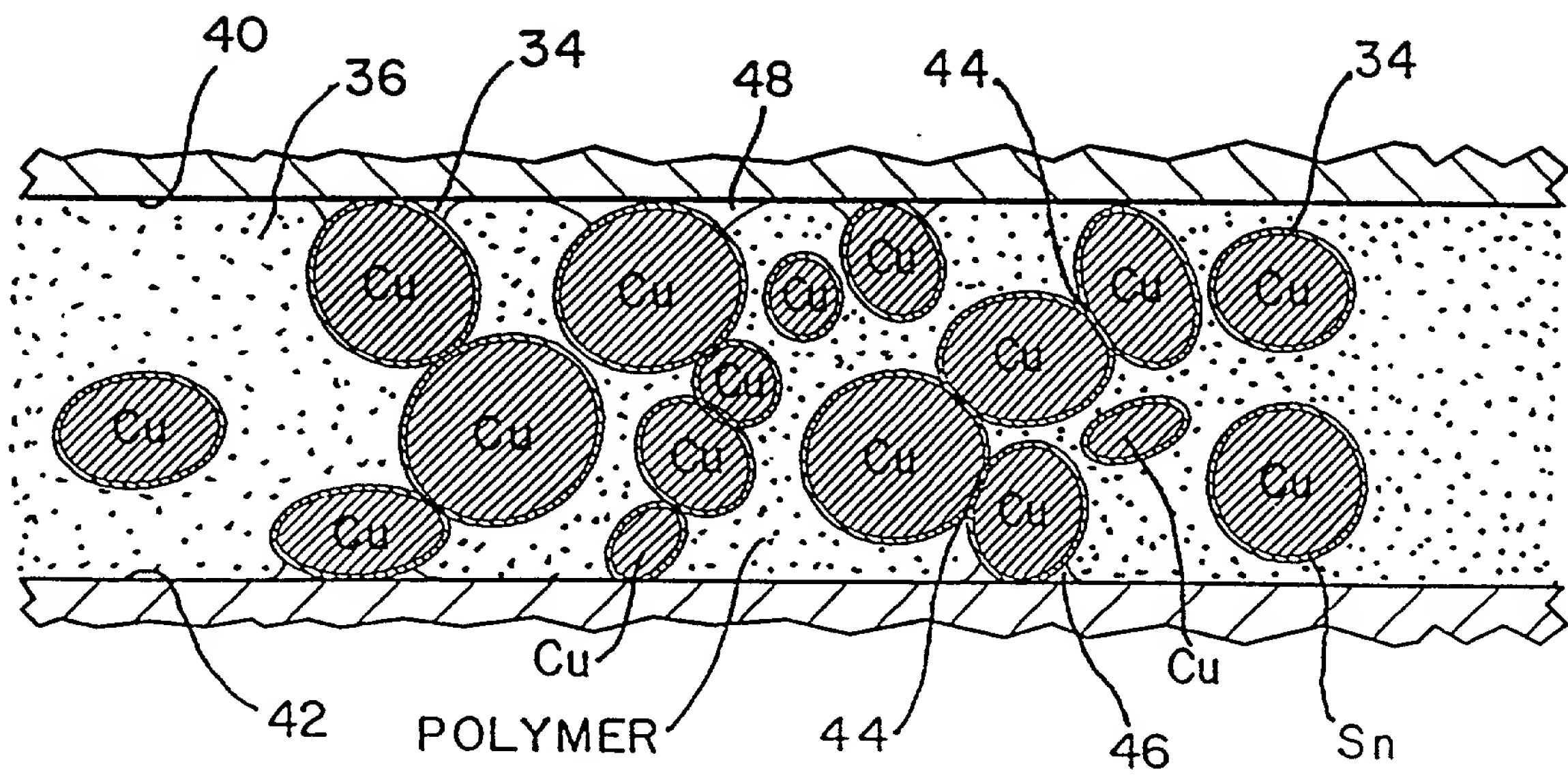


FIG. 3

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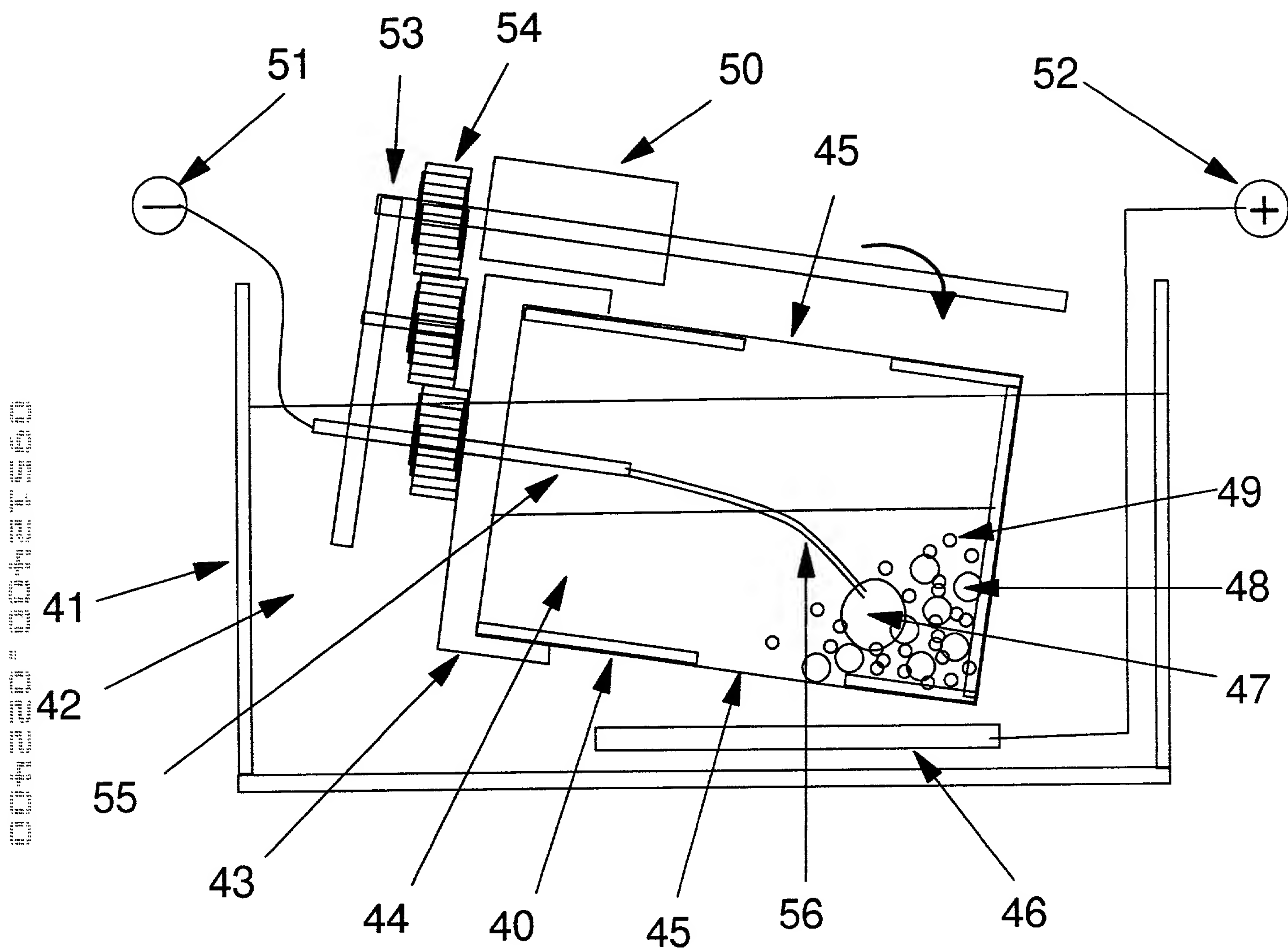


Figure 4



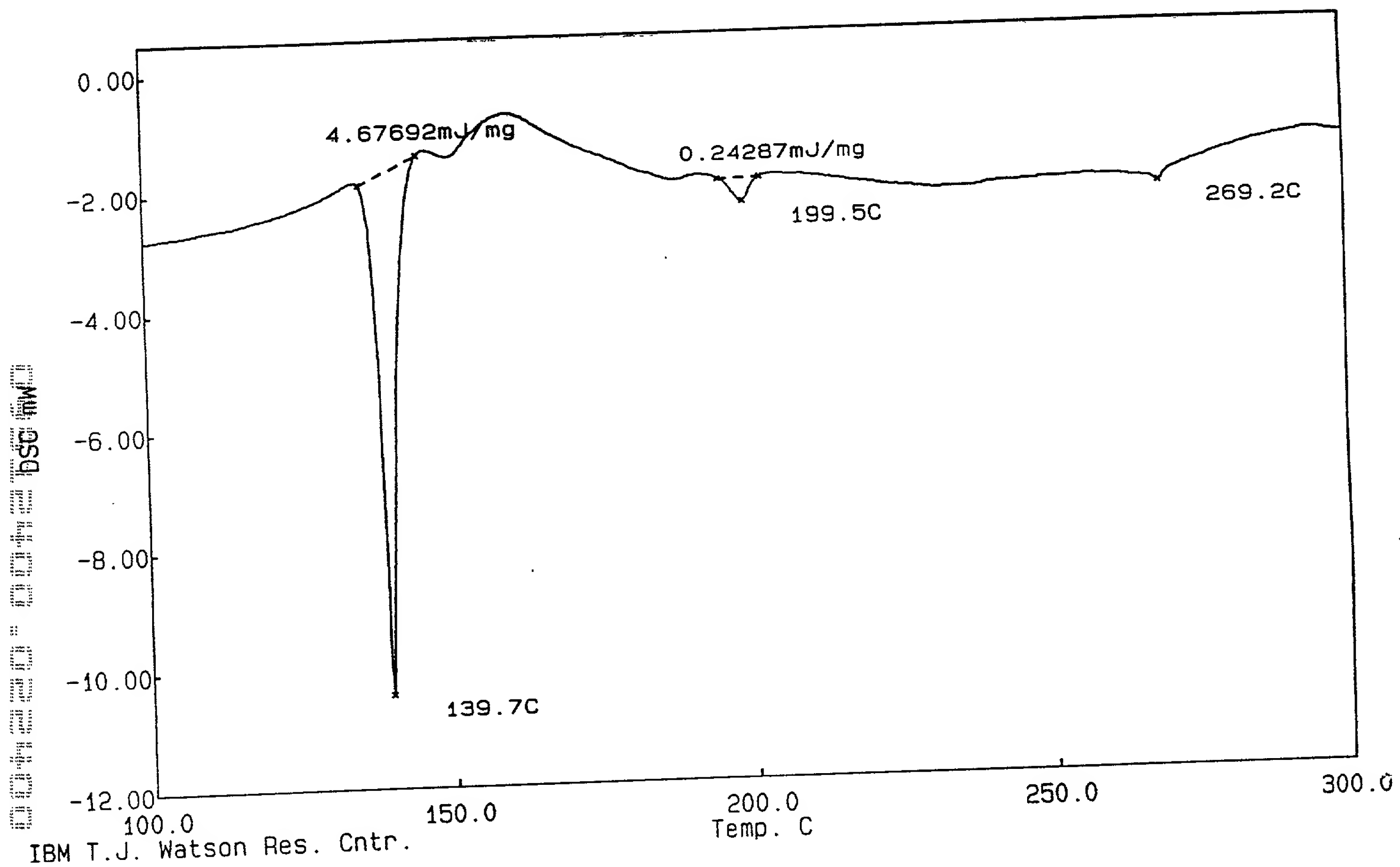


Figure 5

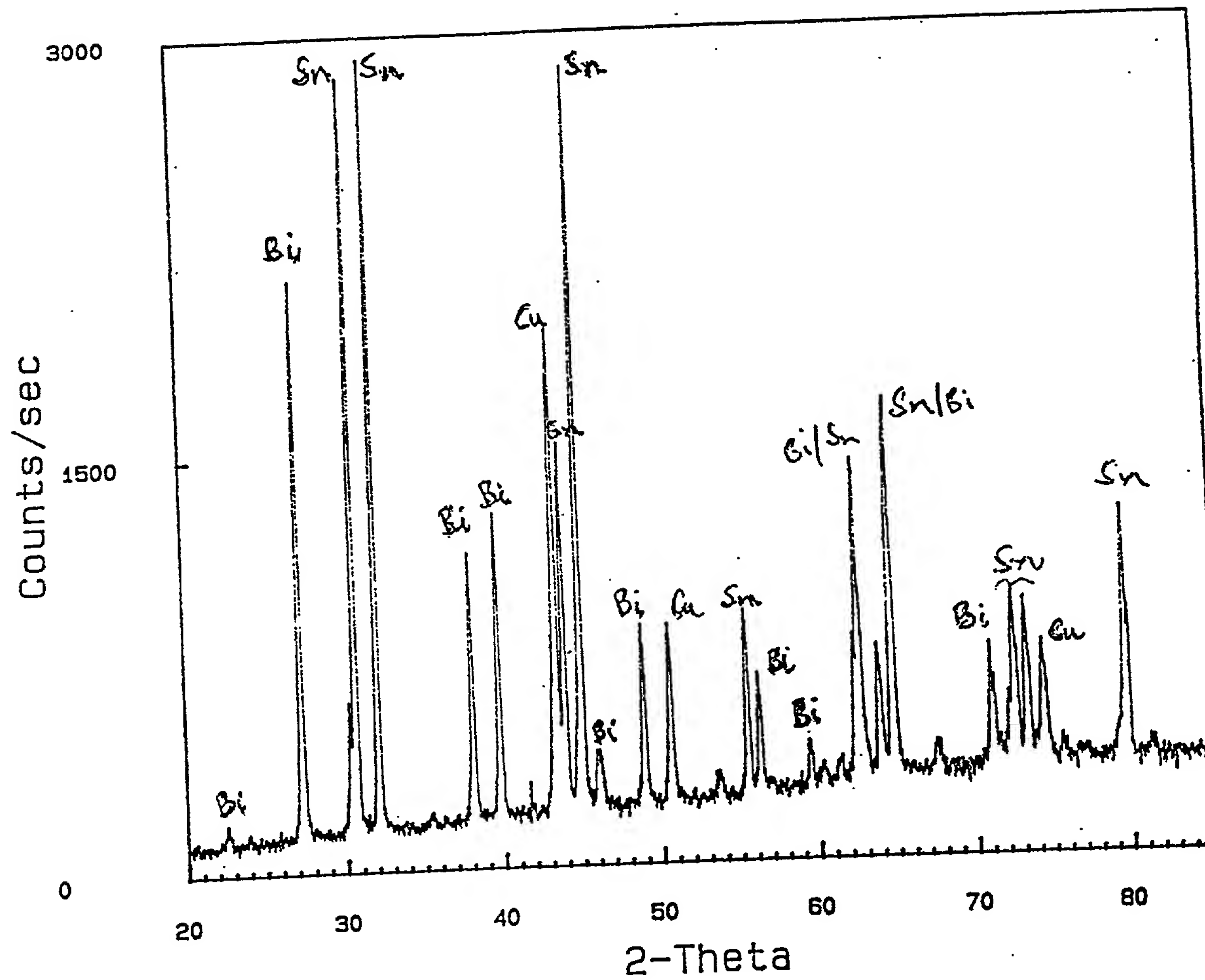


Figure 6